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NO$_x$ ABATEMENT FOR STATIONARY SOURCES IN JAPAN

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16. ABSTRACT The report describes the status of NOx abatement technology for stationary sources in Japan as of August 1976. The report emphasizes flue gas treatment processes for control of NOx. It also features processes for the simultaneous removal of NOx and SOx from flue gases. It examines the major Japanese dry and wet processes, with respect to their applications, performance, economics, major technical problems, developmental status, byproducts, and raw materials. It discusses the application of dry processes, primarily selective catalytic reduction of NOx with ammonia, to commercial scale gas- and oil-fired sources. It presents a review of NOx combustion modification technology in Japan, along with background information on NO2 ambient concentrations, NO2 ambient standards, and NOx emissions standards in Japan. The fact that NOx abatement technology in Japan is the most advanced in the world is probably the result of the NO2 ambient standard in Japan's being the most stringent in the world.

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Flue Gases		Japan	21B	
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PREFACE

This report describes recent developments in NO_x control technology in Japan through May 1976, with emphasis on flue gas denitrification. Flue gas denitrification is considered necessary because the stringent Japanese ambient standard for NO_2 (0.02 ppm in a daily average) cannot be attained by combustion control at stationary sources and by the regulation of automobile exhausts. Many commercial flue gas denitrification plants are in operation and under construction, and many new processes are being developed.

Section 1 of this report introduces the NO_x problem in Japan. This section describes NO_x sources, emission regulations, ambient standards, and ambient concentrations in Japan. It also presents the estimated costs of controlling emissions from stationary sources to achieve the ambient standard.

Section 2 reviews combustion modification technology, particularly for sources firing oil, which has been the major fuel in Japan.

Section 3 describes dry denitrification processes, mainly selective catalytic reduction using ammonia, and the performance of the commercial plants.

Section 4 reviews wet denitrification processes, including many new processes for simultaneous removal of SO_2 and NO_x.

Section 5 discusses the significance of flue gas denitrification and the advantages and disadvantages of many combination systems of flue gas desulfurization and denitrification.

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CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

The metric system is used in this report. Some of the factors for conversion between the metric and English systems are shown below:

1 m (meter) = 3.3 feet
$1\ m^3$ (cubic meter) = 35.3 cubic feet
1 t (metric ton) = 1.1 short tons
1 kg (kilogram) = 2.2 pounds
1 liter = 0.26 gallon
1 kl (kiloliter) = 6.29 barrels
1 kcal (kilocalorie) = 3.97 Btu

The capacity of NO_x removal systems is expressed in normal cubic meters per hour (Nm^3/hr). One Nm^3/hr = 0.59 standard cubic foot per minute. For monetary conversion, the exchange rate of 1 dollar = 300 yen is used.

ABBREVIATIONS

ESP	electrostatic precipitator
kW	kilowatt
kWh	kilowatt hour
LNG	liquefied natural gas
MW	megawatt
SCR	selective catalytic reduction
SV	space velocity

SECTION 1

INTRODUCTION TO NO_x REGULATIONS IN JAPAN

AMBIENT CONCENTRATIONS AND STANDARDS

In 1973 the Japanese government set an ambient standard for NO_2 more stringent than in any other country of the world: 0.02 ppm in a daily average of hourly values, which is roughly equivalent to 0.01 ppm in a yearly average. Conformance with this standard is to be attained within 5 years in most districts and within 8 years in heavily polluted cities such as Tokyo and Osaka. NO_2 concentrations in large cities range from 0.03 to 0.04 ppm in a yearly average and from 0.2 to 0.06 ppm in a daily average. In January 1975 the Environment Agency reported that in only 3 cities among 147 was the NO_2 level as low as 0.02 ppm or lower (yearly average).

Total man-made emission of NO_x in Japan is now about 2 million tons yearly. About 65 percent of the total emission is derived from stationary sources; in large cities, however, 60 to 70 percent is derived from mobile sources.

EMISSION STANDARDS

NO_x emission standards for large stationary sources were first issued in August 1973 (Table 1). These standards

Table 1. NO_x EMISSION STANDARDS FOR STATIONARY SOURCES ISSUED IN 1973 and 1975

(ppm)

Source	Capacity, Nm^3/hr	For new plants		For existing plants		O_2 in gas, %
		1975	1973	1975	1973	
Boiler (gas)	More than 100,000	100	130	130	170	5
	40,000 - 100,000	130	130	130	n	
	10,000 - 40,000	130	n	150	n	
Boiler (solid)	More than 100,000	480	480	750	750	6
	40,000 - 100,000	480	480	750	n	
	10,000 - 40,000	480	n	750	n	
Boiler (oil)	More than 100,000	150	180	230	230	4
	40,000 - 100,000	150	180	190	n	
	10,000 - 40,000	150	n	n	n	
Metal-heating furnace	More than 100,000	100	200	220	220	11
	40,000 - 100,000	150	200	220	220	
	10,000 - 40,000	150	200	200	n	
Heating furnace	More than 100,000	100	170	210	210	6
	40,000 - 100,000	100	170	210	210	
	10,000 - 40,000	150	170	180	n	
Cement kiln	More than 100,000	250	n	n	n	
Coke oven	More than 100,000	200	n	n	n	

n No regulation.

take into account the status of abatement technology -- tail-gas treatment at nitric acid plants and combustion control for other plants -- and are similar to those in the United States. The emission standards were later achieved through 2 years of effort, but the ambient NO_2 concentrations were still much higher than the ambient standard. As a result, new emission standards were promulgated in December 1975 (Table 1). To meet the new standards a considerable number of plants are required to use, in addition to combustion control, low-nitrogen oil or gas in place of the cheap, grade-C heavy oil that is rich in nitrogen. The 1975 standard is applied to about 3000 plants, whereas the 1973 one was applied to about 1000 plants.

The NO_x emission standard for new automobiles weighing over 1000 kilograms is 1.2 grams per kilometer and is equivalent to that in California for 1975 and 1976 models. The standard for new, smaller automobiles is 0.84 gram per kilometer. Those figures will be vastly reduced in the near future because of recent improvements in the technology to reduce NO_x emissions from automobiles.

A serious problem in Japan is that the ambient standard will be far out of reach even when the new emission standards are attained. Flue gas denitrification is thus needed not only for NO_x-rich tail gas from plants producing or using nitric acid but also for flue gas from numerous plants using fossil fuels.

AIR POLLUTION CONTROL AGREEMENT IN CHIBA PREFECTURE

Most prefectural governments have made agreements with local industries for pollution control. An example of reductions expected in the Chiba prefecture is shown in Table 2. Chiba is close to Tokyo and has one of the largest industrial complexes in Japan. The agreement was made in February 1976 with 40 companies that have 45 large plants in the complex. SO_2 emissions from those plants will be reduced from 13,395 Nm^3/hr in 1973 to 4706 Nm^3/hr in 1977 in order to attain the national ambient standard for SO_2, namely, 0.04 ppm daily average. NO_x emissions will be reduced from 9668 to 5119 Nm^3/hr in the same period. In addition to combustion modification and change of fuel, flue gas denitrification is required for several large boilers, several heating furnaces, and a few iron-ore sintering plants and coke ovens. As a result of these efforts ambient NO_2 concentrations will decrease to 0.04 ppm daily average, an intermediate goal. However, to attain the national ambient standard of 0.02 ppm daily average, the NO_x emissions from these sources will have to be reduced to about 2700 Nm^3/hr.

Table 2. EXPECTED REDUCTION OF AIR POLLUTANTS IN CHIBA PREFECTURE DUE TO AGREEMENTS WITH INDUSTRIES

Type of industry	Number of plants	SO_x			NO_x			Particulates		
		Nm^3/hr		Reduction, %	Nm^3/hr		Reduction, %	kg/hr		Reduction, %
		1973	1977		1973	1977		1973	1977	
Power	6	6,150	1,745	71.6	5,218	2,427	53.5	822	244	70.4
Steel	2	3,010	1,159	61.5	1,930	1,142	40.8	670	285	57.0
Oil refining	4	2,098	645	69.3	1,043	568	45.6	478	220	54.1
Petrochemical	14	1,414	858	39.3	1,066	690	35.3	289	231	18.0
Chemical	12	510	207	59.4	248	184	26.0	223	92	58.8
Other	7	214	92	56.7	163	110	32.7	48	32	34.0
Total	45	13,395	4,706	64.9	9,668	5,119	47.1	2,531	1,108	56.2

COST OF NO_x ABATEMENT TO ATTAIN AMBIENT STANDARD (12)

In October 1975 the Nitrogen Oxides Investigation Committee of the Environment Agency published a report describing the estimated cost to stationary sources for NO_x abatement to attain the ambient standard. For convenience of cost estimation, Japan was divided into four regions:

A. Large cities (Tokyo, Osaka, Nagoya, Chiba, etc.)

B. Industrial districts (Kashima, Toyama, Fuji, Handa, Yokkaichi, Omuta, Kitakyushu, etc.)

C. Middle-size cities (Kyoto, Sapporo, Sendai, Okayama, etc.)

D. Other districts.

NO_x emissions and abatement required for each region are shown in Table 3. Table 4 lists the amounts of fuels required for boilers and furnaces in 1980 without control and with control to attain the ambient standard. Costs of the fuels are given in Table 5.

Table 3. ESTIMATED NO_x EMISSIONS FROM BOILERS AND FURNACES (10^6 Nm^3/year)

	A	B	C	D	Total
1973	181.2	207.8	23.2	179.5	591.7
1980 (without control)	237.6	272.5	30.4	235.3	775.8
1980 (with control)	49.9	98.1	12.2	117.7	277.9
Abatement ratio, %	79	64	60	50	64

Table 4. CONSUMPTION OF FUELS BY BOILERS AND FURNACES (kl/year)

Fuel	Without control	With control
High-sulfur heavy oil	72,400	49,300
Medium-sulfur heavy oil	101,500	53,100
Low-sulfur heavy oil	24,800	33,000
Kerosene, naphtha	2,500	16,400
Gas	15,600	65,000
Coal	11,200	11,200
Total	228,000	228,000

Table 5. COSTS OF FUELS

Fuel	Cost, $/kl or kl equivalent
High-sulfur heavy oil ($S \geq 1.5$)	66.7
Medium-sulfur heavy oil ($0.5 \leqq S \leqq 1.5$)	83.3
Low-sulfur heavy oil ($0.1 \leqq S \leqq 0.5$)	100.0
Kerosene ($S < 0.1$)	106.7
Gas (For plants larger than 40,000 Nm^3/hr)	116.7
Gas (For smaller plants)	150.0

The costs of flue gas desulfurization and denitrification are based on the assumptions shown in Table 6.

Table 6. ASSUMED COSTS OF FLUE GAS DESULFURIZATION AND DENITRIFICATION

	Investment		Annual cost*	
	$\$/Nm^3/hr$	\$/MW	$mills/Nm^3$	mills/kWh
Desulfurization	23.2	70	1.25	3.75
Denitrification	33.3	100	2.43	8.29

* Including depreciation (7 years) and interest (10% per annum) at 70% operation.

Table 7 summarizes the estimated cost of NO_x control for boilers and furnaces based on the above assumptions. The investment costs are \$5810 million for denitrification and \$1844 million for desulfurization. The annual costs are \$2950 million for denitrification and \$680 million for desulfurization. A change of fuel will require an additional cost of \$2596 million, whereas combustion modification costs only \$464 million in investments and \$92 million in annual costs. The total investment cost reaches \$8118 million, and the total annual cost reaches \$6318 million.

In addition, NO_x abatement is required for other large stationary sources, such as iron-ore sintering plants, coke ovens, glass melting furnaces, and cement kilns. The costs for those sources will be about \$1700 million in investments and \$850 in annual costs.

Table 7. ESTIMATED COST OF NO_x ABATEMENT FOR BOILERS AND FURNACES

(millions of dollars)

	Region classification				Total
	A	B	C	D	
(No. of plants)	(1260)	(123)	(65)	(71)	(1519)
NO_x control					
Fluc gas denitrification					
Investment cost	3870	1033	247	660	5810
Annual cost*	1903	567	117	363	2950
Combustion modification					
Investment cost	90	147	27	200	464
Annual cost*	13	43	3	33	92
SO_2 control					
Flue gas desulfurization					
Investment cost	767	947	27	103	1844
Annual cost*	283	350	10	37	680
SO_2 - NO_x control					
Change of fuel					
Annual cost *	903	1193	120	380	2596
Total investment cost	4727	2127	301	963	8118
Total annual cost*	3102	2153	250	813	6318

* Annual cost includes depreciation (7 years), interest (10% per annum), labor, fuel, etc.

Although recent progress in denitrification technology has reduced denitrification costs below those in Table 6, extremely large expenditures will still be needed to attain the NO_2 ambient standard.

The Environment Agency intends to re-estimate the costs more precisely to allow public evaluation of NO_x abatement programs.

SECTION 2

NO_X ABATEMENT BY COMBUSTION CONTROL

CLASSIFICATION OF COMBUSTION CONTROL TECHNIQUES

Combustion modification techniques used in Japan for NO_x control can be classified into the following three categories:

(1) Change of Operating Conditions

- Low excess-air combustion
- Promotion of mixing of fuel with air in combustion chamber
- Reduction of heat load in combustion chamber
- Less air preheating

(2) Modification of Combustion System Design

- Modifications of burner design
- Staged combustion
- Flue gas recirculation
- Water or steam injection

(3) Other Methods

- Change of fuel
- Modification of firing

Although changes of operating conditions can be relatively easy at existing installations, they usually reduce the NO_x emissions only slightly and often cause operating difficulties. On the other hand, modification of the combustion system design is a promising control technique.

Fewer problems are encountered when design modifications are incorporated in new plants; whereas, relatively large reconstruction costs are required when they are applied to existing installations.

NO_x emissions from combustion processes are formed by two mechanisms: thermal NO_x (that generated in the combustion process) and fuel NO_x (that attributable to nitrogen content of the fuel). Formation of thermal NO_x can be suppressed effectively by decreasing the oxygen concentration in the combustion regions, by shortening the residence time of combustion gases in the high temperature zones, or by lowering the flame temperature. Reduction of fuel NO_x emissions requires reducing both the oxygen concentration in the reaction zone and the nitrogen content of the fuel.

CHANGE OF OPERATING CONDITIONS

Low Excess-Air Combustion

Low excess-air combustion (0.6 - 1.0% O_2 in flue gas from oil burning) has been used in large boilers for several years to reduce the SO_3 that causes low-temperature corrosion. Low excess-air combustion is also useful in NO_x abatement, particularly with large boilers burning high-nitrogen fuels, such as grade B (0.08 - 0.35% N) or grade C (0.25 - 0.35% N) heavy oil. The technique is not widely used with small boilers, which usually burn low-nitrogen fuels such as kerosene, grade A heavy oil, or gas. The small boilers normally are unmanned, and their operation is not very well controlled. Therefore, operation with low excess air in these boilers tends to cause incomplete combustion.

Promotion of Mixing of Fuel with Air in Combustion Chamber

It has been reported that a considerable NO_x reduction is achieved through a slight adjustment of the air register; for example, a change in the vane angle. Very few existing installations use this technique. Changing the air system makes it necessary to readjust the air fuel mixture. An improper adjustment may increase the quantity of unburned products such as soots, carbon dioxide, and hydrocarbons, or it may cause unstable combustion. In new boilers and also in existing ones, the air register is often modified when a low-NO_x burner is installed.

Reduction of Heat Release Rate in the Combustion Chamber

NO_x emissions can also be reduced by decreasing the boiler load. The use of this method in existing installations, however, results in a decrease in fuel efficiency and output power. Therefore, this method is regarded as an emergency measure, to be applied, for example, when the ambient oxidant concentration exceeds 0.3 or 0.5 ppm and the prefectural governor issues a recommendation or order to decrease fuel consumption.

Manufacturers currently are designing boilers with lower heat release rates than those of older ones. The new boilers are larger and more easily adaptable to such NO_x control techniques as two-stage combustion.

Less Air Preheating

A reduction in air preheating temperature reduces the flame temperature and consequently the formation of thermal NO_x. This method is seldom used because it also reduces boiler efficiency. Moreover, application is limited to large boilers with air preheaters, for which better control techniques are available.

MODIFICATION OF COMBUSTION SYSTEM DESIGN

Modification of Burner Design

Low-NO_x burners developed in Japan may be classified into the following four types, based on the NO_x suppression principles and burner configuration:

(1) Good-mixing type,
(2) Divided-flame type,
(3) Self-recirculation type,
(4) Staged-combustion type.

Good-mixing and divided-flame type burners are useful in reducing formation of thermal NO_x but have little effect in reducing fuel NO_x. Self-recirculation and staged-combustion types, by contrast, seem to reduce emissions of both types of NO_x.

Since three of the categories -- good mixing, divided flame, and self recirculation -- were discussed in earlier reports (1,2) only the staged-combustion type burners are described here. There are two types of staged-combustion burners: the two-stage combustion type and the off-stoichiometric combustion type. A two-stage combustion type burner (Figure 1) has been developed by Tokyo Gas Company for the firing of town gas. A more advanced burner of this type burner has a catalyst at the outlet of the preliminary combustion region for further reduction of NO_x (3). Figure 2 shows the emission levels with this burner. HCN and NH_3 are likely to play a significant role in NO_x formation in the second stage. The catalyst reduces HCN and NH_3 together with NO_x (Figure 3). These burners are not yet used commercially because of problems such as flashback.

The configuration of the two-stage combustion burner fired with oil is illustrated in Figure 4 (4). This type, with a precombustion chamber, is designed by Kawasaki Heavy Industries. The chamber is installed in the wind box, and the second-stage air inlet is placed at the end of the chamber. Oil is fired in the chamber with an insufficient amount of air. Vaporization of the oil results from the high temperatures of circulating gas and of the refractory. Considerable reduction of both forms of NO_x is thus attained.

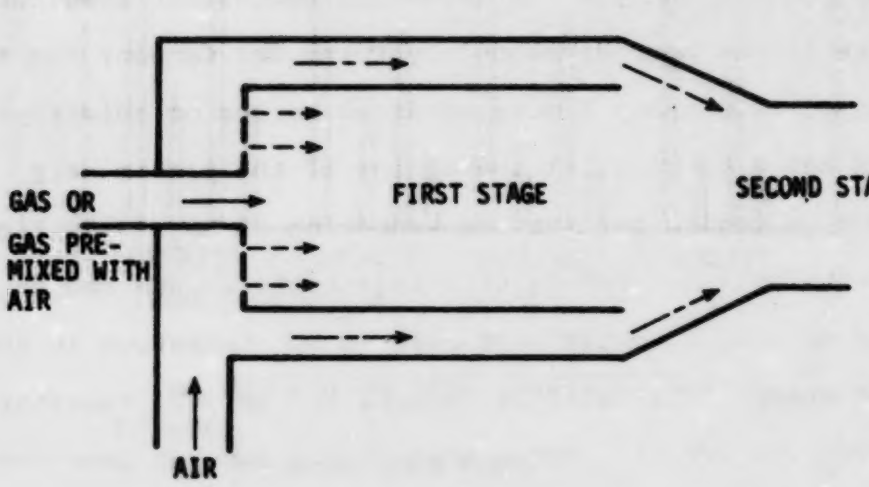

GAS OR
GAS PRE-
MIXED WITH
AIR
FIRST STAGE
SECOND STAGE
AIR

Figure 1. Two-stage combustion type burner for low-NO_x formation.

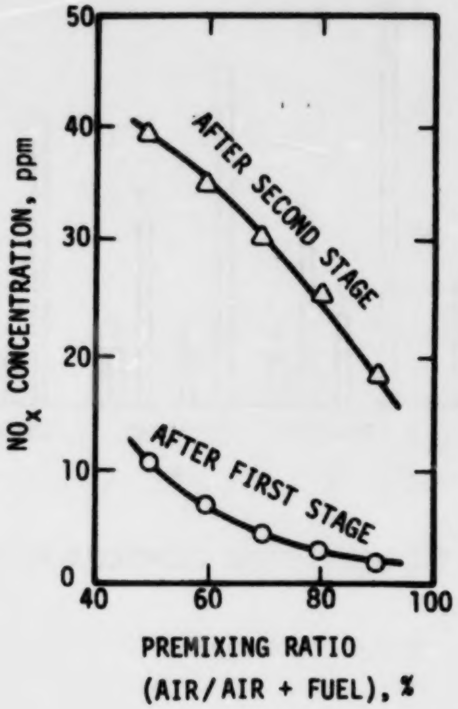


Figure 2. NO_x emission from the low-NO_x burner shown in Figure 1.

(Fuel, methane; thermal input, 95,000 kcal/hr; NO_x concentration corrected to 0% O_2)

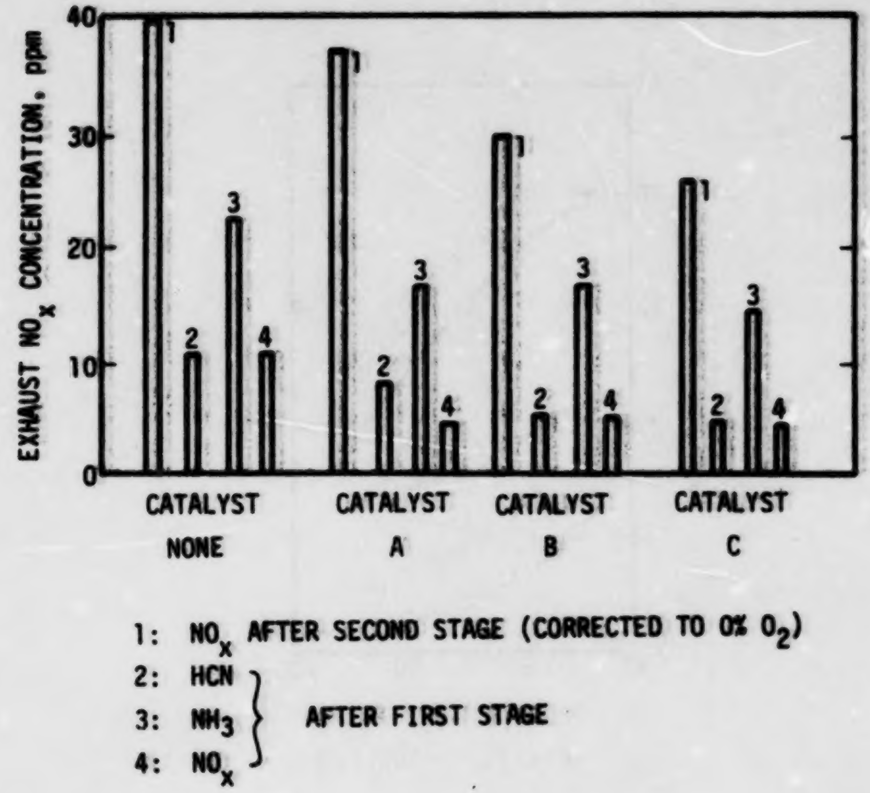


Figure 3. Effect of catalyst on NO_x emissions from two-stage combustion burner.

(Fuel, methane; thermal input, 95,000 kcal/hr; sv, 65 hr^{-1}; premixing ratio, 0.50; equivalent ratio in first stage, 1.67)

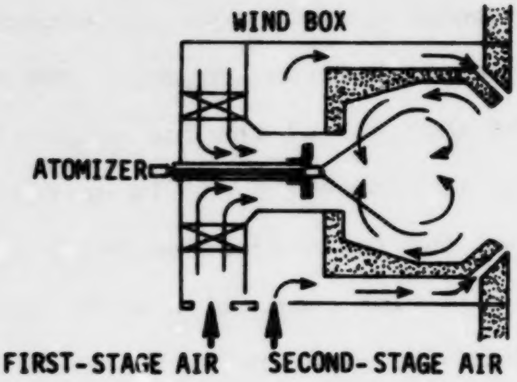

WIND BOX
ATOMIZER
FIRST-STAGE AIR
SECOND-STAGE AIR

Figure 4. Two-stage combustion-type burner for oil.

NO_x concentrations from this burner are compared with those from a conventional burner in Figure 5.

An off-stoichiometric combustion type burner for gas-firing was mentioned in a previous report (1). Figure 6 shows arrangement of the fuel-injection holes of atomizing nozzles in an off-stoichiometric combustion burner for oil-firing (5), developed by Volcano Company. The main feature of this atomizer is that all of the fuel-injection holes are not the same size. As combustion air is uniformly admitted around the atomizer, the fuel-injection holes with larger diameters produce fuel-rich combustion zones whereas the smaller holes produce fuel-lean regions. Therefore, off-stoichiometric combustion is achieved.

Several different arrangements of fuel-injection holes are available. The optimum arrangement may be determined by experimentation. Because of the ease of installation and the low cost, this burner has been used widely. In some cases, altering only the nozzle tips can successfully reduce NO_x emissions. NO_x levels produced by such a burner are shown in Figure 7. This burner tends to increase soot emissions when excess air is low because some of the flame zones are deficient in oxygen.

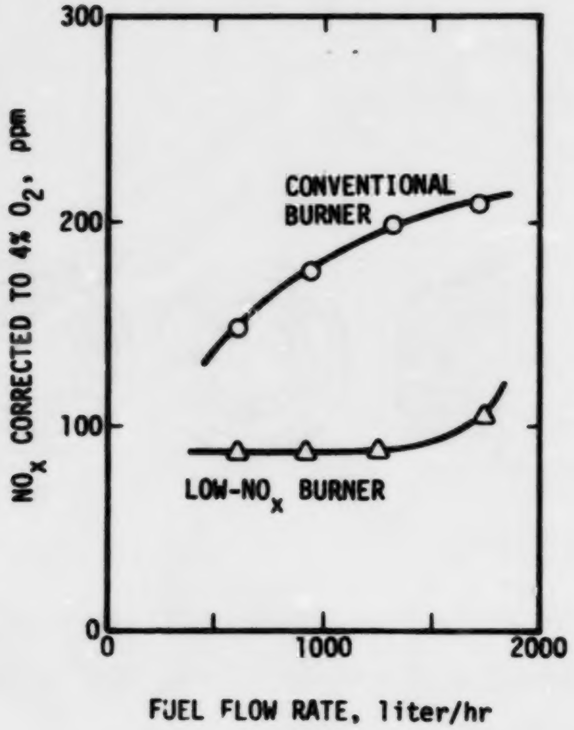


Figure 5. Effect of low-NO$_x$ burner on NO$_x$ emissions.

(Fuel, grade C heavy oil; N = 0.206%)

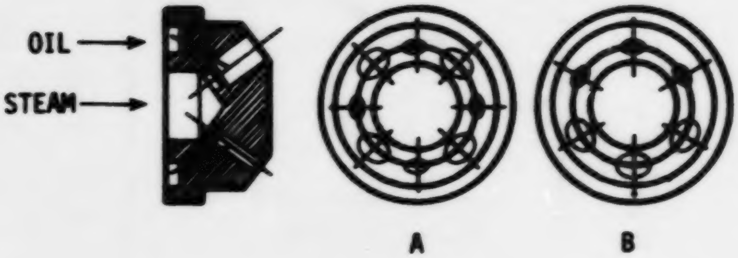

OIL
STEAM
A
B

Figure 6. Atomizing nozzles in off-stoichiometric combustion-type low-NO_x burner for oil.

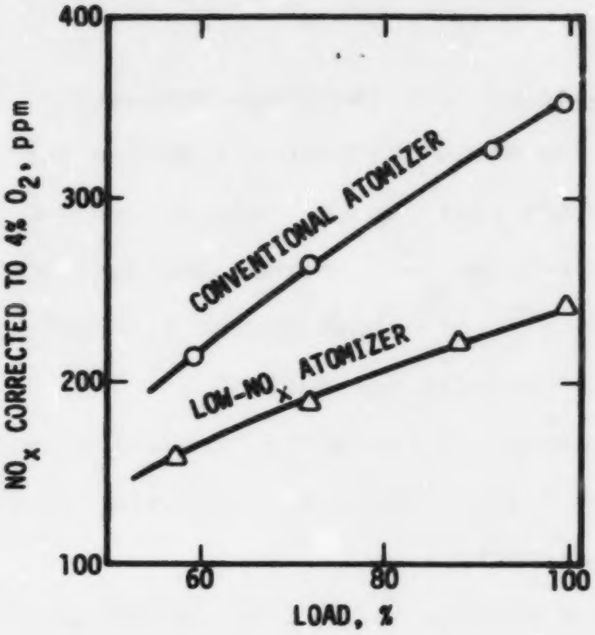


Figure 7. Effect of low-NO_x atomizer on NO_x emissions.

(Boiler capacity, 55 t/hr; fuel, grade C heavy oil; air temperature, 280°C; four atomizers)

Staged Combustion

There are two major categories of staged combustion: two-stage (the numbers of stages seldom exceed two) and off-stoichiometric.

Two-stage combustion - In two-stage combustion, about 80 to 90 percent of the stoichiometric air needed for combustion is admitted to the first stage. Oxygen-starved combustion in this region reduces both thermal and fuel NO_x. Reduction efficiencies usually are about 30 to 50 percent for thermal and less than 50 percent for fuel NO_x.

The application of two-stage combustion is classified into four types determined by the following locations of second-stage air ports.

1) On the furnace wall above the burners.
2) Top burners for air injection only.
3) Side or rear walls of the furnace.
4) On the circumference of the burners.

Large utility boilers employ types 1) or 2). Type 2), called quasi-two-stage combustion, is used in units to which type 1) cannot be applied (6). Types 3) and 4) are used in medium and small boilers. Type 3) is not popular for water tube boilers because it requires considerable remodelling. Type 4), as illustrated in Figure 8, can be readily applied to small installations with a single burner because it

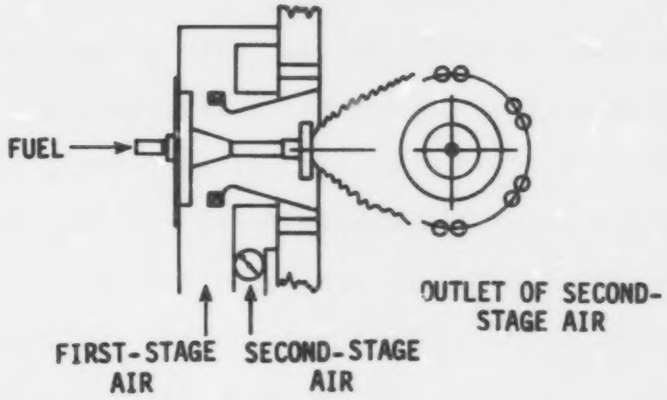

FUEL
OUTLET OF SECOND-STAGE AIR
FIRST-STAGE AIR
SECOND-STAGE AIR

Figure 8. Two-stage combustion for small boiler.

requires little remodelling. Two-stage combustion cannot be applied to installations with furnace dimensions that cannot accomodate the greater flame length. Also two-stage combustion tends to increase the amount of unburned products, particularly CO (7).

Off-stoichiometric Combustion - This method has an effect similar to that of two-stage combustion and is readily adapted to medium and small boilers with several burners, to which two-stage combustion is not easily applied.

Location of fuel-rich and fuel-lean burners or air ports is decided after systematic tests. Often, it is effective to place the fuel-lean burners or air ports in the central upper parts of furnace walls above the burners, or in the regions of highest heat release (6).

Flue Gas Recirculation

In flue gas recirculation, NO_x reduction is achieved through the decrease of flame temperature. Thus, fuel NO_x is not reduced, but thermal NO_x is reduced by 30 to 40 percent. Recirculation ratios are limited to about 30 to 40 percent to prevent unstable firing, although this limit is lower with larger units. Keeping the recirculation ratios in suitable ranges may improve combustion conditions and decrease the quantities of unburned products. however, the decrease of flame temperature alters the distribution of heat transfer and lowers the fuel efficiency of existing boilers.

A recirculation fan and additional duct work are required to implement flue gas recirculation. As a result, installation cost is considerably higher than that for two-stage combustion and more installation space is required. Therefore, this method is not used with small boilers or furnaces. Many operators of large boilers recirculate flue gases because of the stabilizing effect, which reduces operational problems.

Water or Steam Injection

Water or steam injection reduces NO_x emissions by decreasing the flame temperature. There are three injecting methods:

a) Injecting into the combustion air.

b) Injecting into the combustion chamber. (This includes increasing the steam flow rate in the steam atomizer.)

c) Mixing water with the fuel (emulsification).

With an equal injection rate, b) and c) offer greater NO_x reduction than a) because of the greater reduction in flame temperature. The injection ports close to the burners are effective for b). The upper injection rate limit is about 5 kg/10^4 kcal (8).

With the use of this technique, combustion characteristics are improved, making it possible to reduce excess air; therefore, the decease in thermal efficiency may not be very great.

There are two kinds of emulsified fuels: water droplets suspended in oil (W/O type) and oil particles suspended in water (O/W type). The former is used in oil firing because the resulting emulsion viscosity is less than that of an O/W type emulsion.

Figure 9 shows a fuel emulsion system developed by Kawasaki Heavy Industries (4). Oil to which a slight amount of emulsifying agent is added is mixed with water in a mechanical mixer. This emulsified fuel is reserved in a service tank and pumped to the burners.

Since it does not reduce fuel NO_x, this method is useful with low-nitrogen oils. Figure 10 shows NO_x emission levels obtained by using emulsified fuel.

OTHER METHODS

Change of Fuel

Except in special cases, NO_x emissions are related to nitrogen content of the fuel, which decreases in the following order: solid fuels (coal and coke), liquid fuels (petroleum fuel oils), and gaseous fuels (town gas, LNG and LPG).

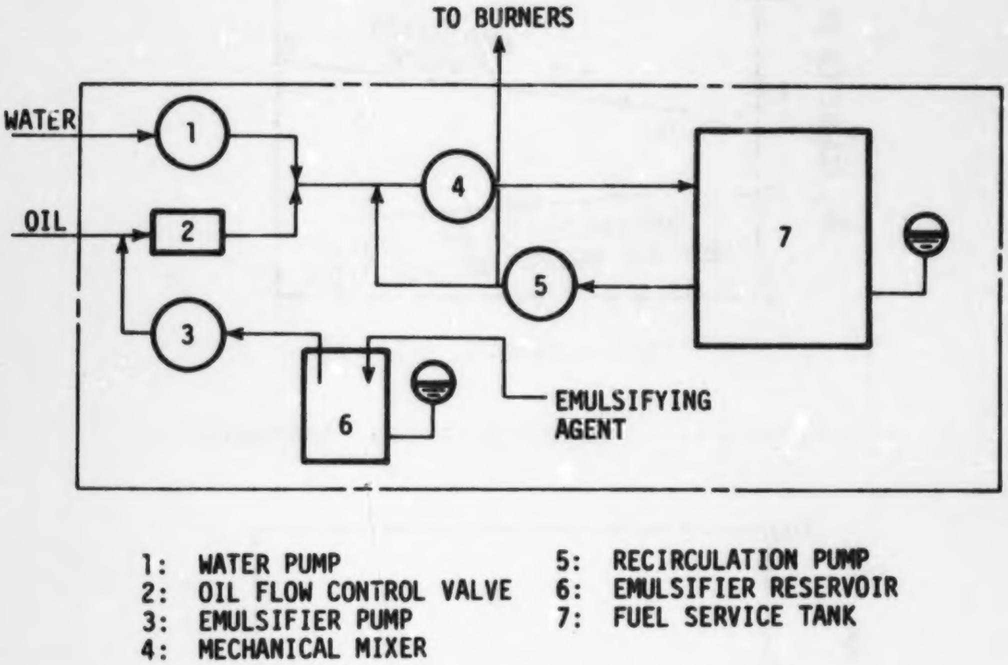

TO BURNERS
WATER
OIL
1
2
3
4
5
6
7
EMULSIFYING AGENT
1: WATER PUMP
2: OIL FLOW CONTROL VALVE
3: EMULSIFIER PUMP
4: MECHANICAL MIXER
5: RECIRCULATION PUMP
6: EMULSIFIER RESERVOIR
7: FUEL SERVICE TANK

Figure 9. Flow diagram of apparatus for producing and supplying emulsified oil.

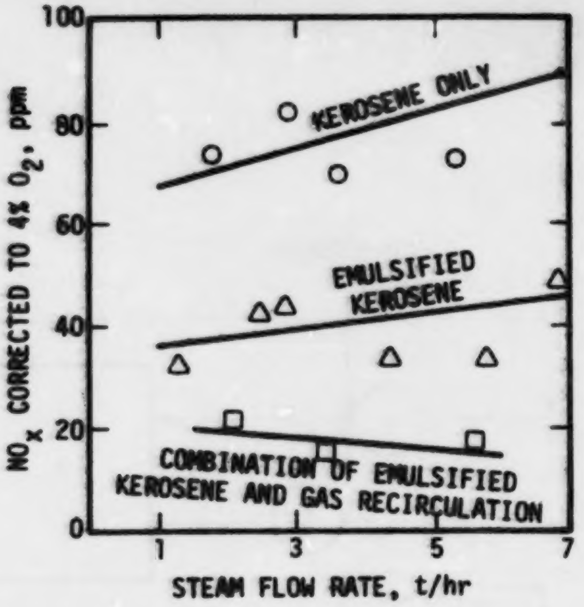


Figure 10. NO$_x$ emission with kerosene.

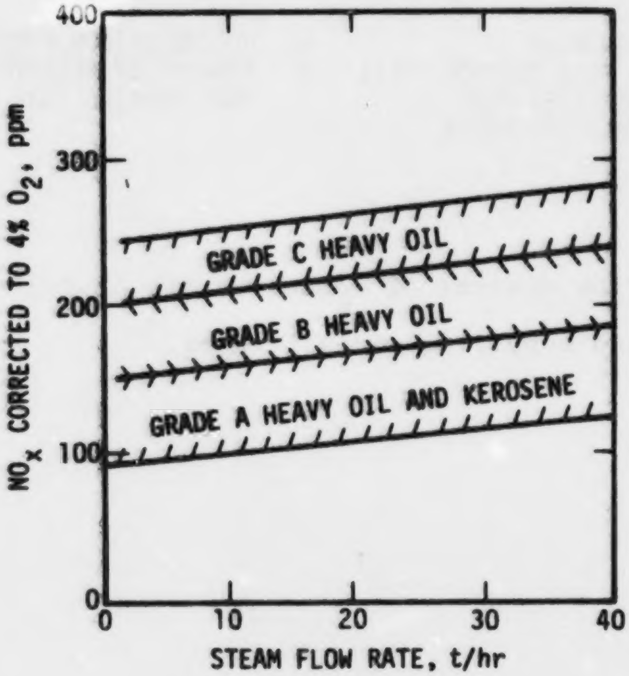


Figure 11. NO$_x$ emission levels in oil-fired boilers.

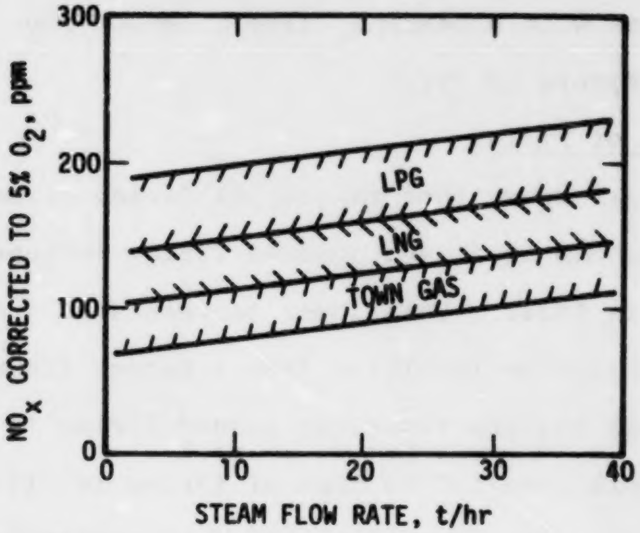


Figure 12. NO$_x$ emission levels in gas-fired boilers.

NO_x emissions are lower with low-nitrogen oil, such as kerosene or grade A heavy oil, than with grade C heavy oil (Figure 11) (9). The emissions from gas burning decrease in the order of LPG (C_3H_8 and C_4H_{10}), LNG (CH_4), and town gas (synthetic gas with a heating value of about 5000 kcal/Nm^3), as shown in Figure 12 (9).

Modification of Firing

It is well-known that tangential firing gives lower NO_x emissions than do front and opposed firing because the flame temperature is lower. This lower temperature is caused by better heat emission resulting from a larger flame volume.

For small boilers reversely turned firing is used to reduce NO_x emissions. This type of firing is illustrated in Figure 13. NO_x reduction is obtained by recirculation in the flue tube.

APPLICATION OF TECHNIQUES

Combination of Techniques

A combination of the above-mentioned techniques can increase the reduction of NO_x emissions. However, a combination of techniques based on the same suppression principles, such as the combination of two-stage and off-stoichiometric combustion, is not efficient.

With large boilers flue-gas recirculation is generally combined with two-stage combustion. With smaller boilers,

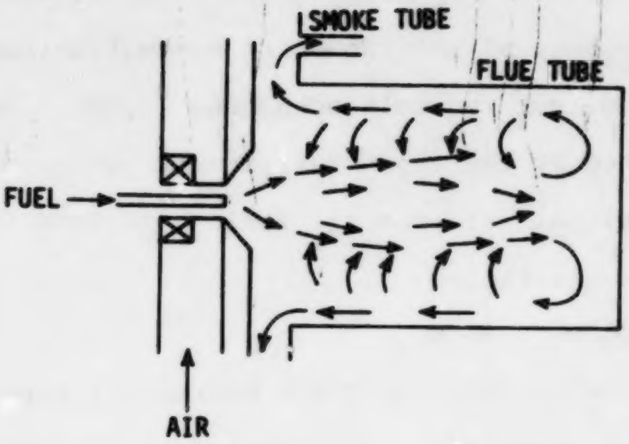

SMOKE TUBE
FLUE TUBE
FUEL
AIR

Figure 13. Air flow in reversely-turned firing.

control techniques similar to those used with large ones are practiced but the use of low-NO_x burners is more popular. Many oil-refining furnaces use a combination of a two-stage combustion and a self-recirculation-type, low-NO_x burner.

Field Tests

Since 1974 the Japan Environment Agency and Tokyo Metropolis Bureau of Environmental Protection have made field tests of NO_x control techniques (7,10). NO_x reductions reported by the Japan Environment Agengy have ranged from 19 to 67 percent with oil firing and from 19 to 73 percent with gas firing.

INVESTIGATION OF FUEL NO_x

From 1974 to 1975 the Tokyo Metropolis Bureau of Environmental Protection investigated the relationship between the nitrogen and sulfur contents of fuel and the fuel NO_x conversion ratio (11).

Figure 14 shows the relationship between the sulfur and nitrogen contents of fuels.

Nitrogen contents of fuels fed to 90 commercial boilers were measured, along with NO_x emissions from those boilers. More detailed tests were done with one boiler to determine the effects of excess air, boiler load, and nitrogen content on the fuel NO_x conversion ratio. These tests showed that nitrogen content was the most significant factor influencing

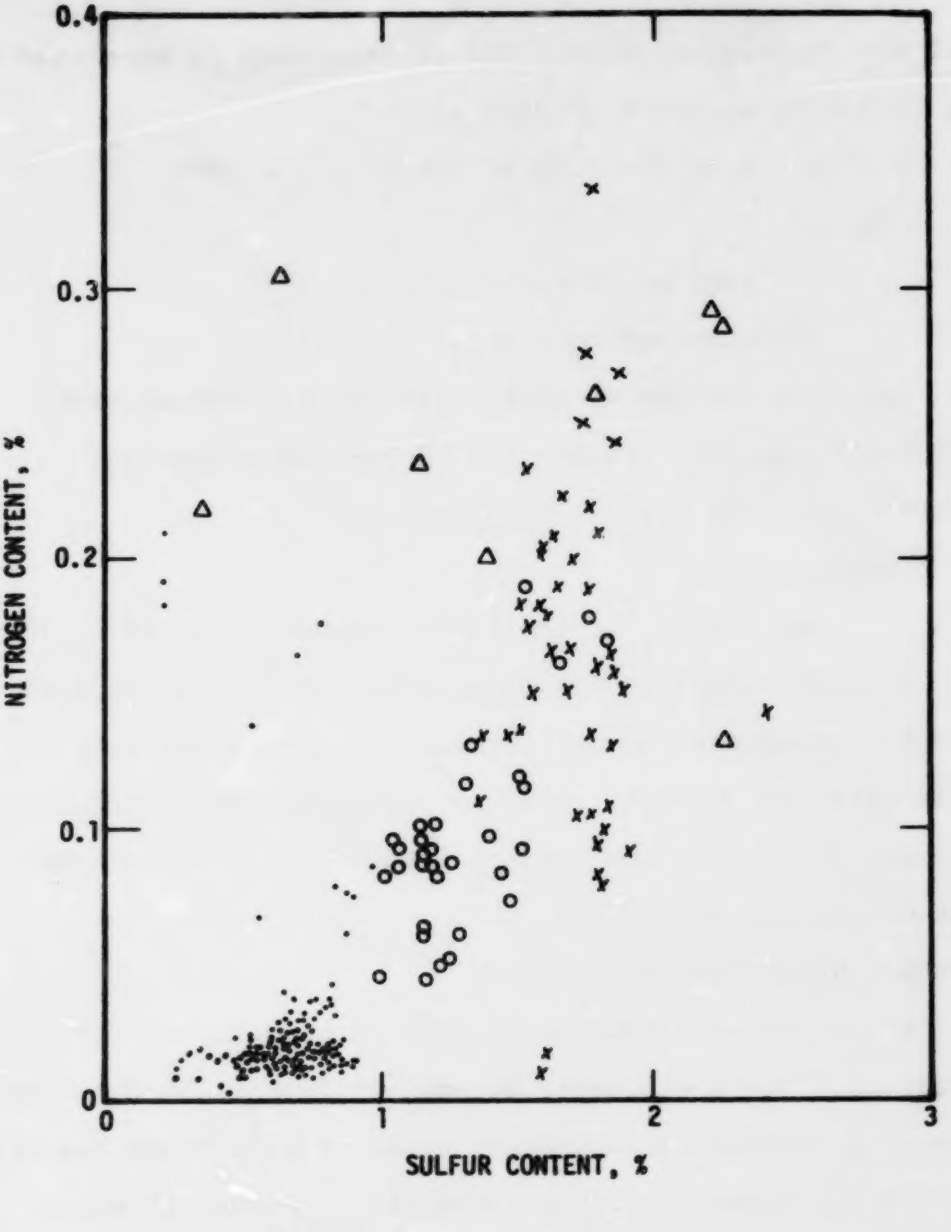


Figure 14. Relation between nitrogen and sulfur contents in heavy oils.

fuel NO_x conversion ratio. The relationship is expressed by the following equation (Figure 15):

$$\alpha = (1 - 4.58\ n + 9.50\ n^2 - 6.67\ n^3) \times 100\%$$

Where

α = Fuel NO_x conversion ratio (%)

n = Nitrogen content in fuel (%)

Applying the above equation to the results of tests with the 90 boilers (Figure 16) yields the following:

$$[NO_x] = 1550\ n\ \frac{\alpha}{100} + 110\ \text{(ppm)}$$

Where

$[NO_x]$ = NO_x concentration corrected to 0% O_2 (ppm)

With this equation it is possible to predict approximate NO_x emissions for boilers burning a fuel oil with a known nitrogen content. When an oil containing 0.2 percent nitrogen is burned, the amount of fuel NO_x is about equal to that of thermal NO_x.

FURTHER INVESTIGATIONS

A low nitrogen content in fuel is significant for NO_x reduction. The Environment Agency has investigated nitrogen removal by hydrodesulfurization of heavy oil, which has been carried out commercially in Japan (11). Figure 17 shows examples of the reductions achieved. About 30 percent of the nitrogen can be removed, but this is generally insufficient to meet emission regulations.

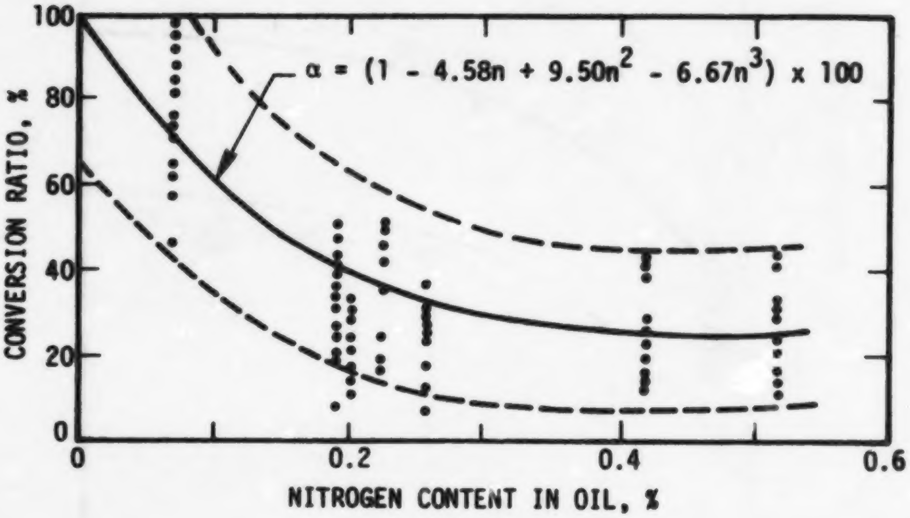


Figure 15. Relation between nitrogen content in oil and fuel NO_x conversion ratio in boiler.

(Steam flow rate, 1 t/hr; load, 40-100%; excess air, 5-100%; base fuel, kerosene and grade B heavy oil; additive containing nitrogen, quinoline and pyridine)

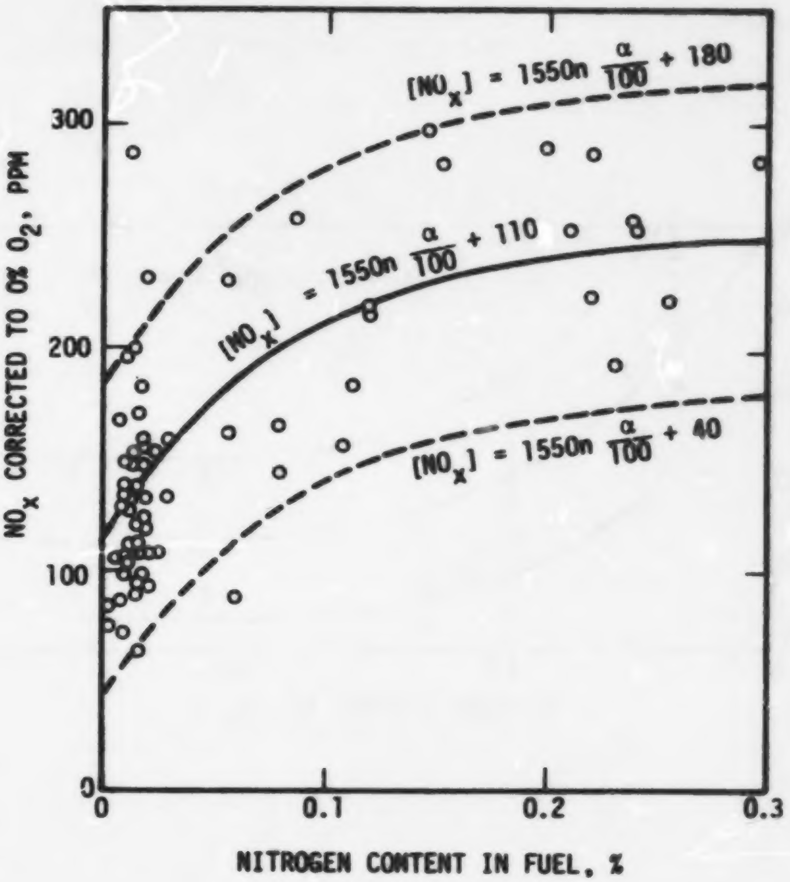


Figure 16. NO_x concentration versus nitrogen contents of fuel in many boilers.

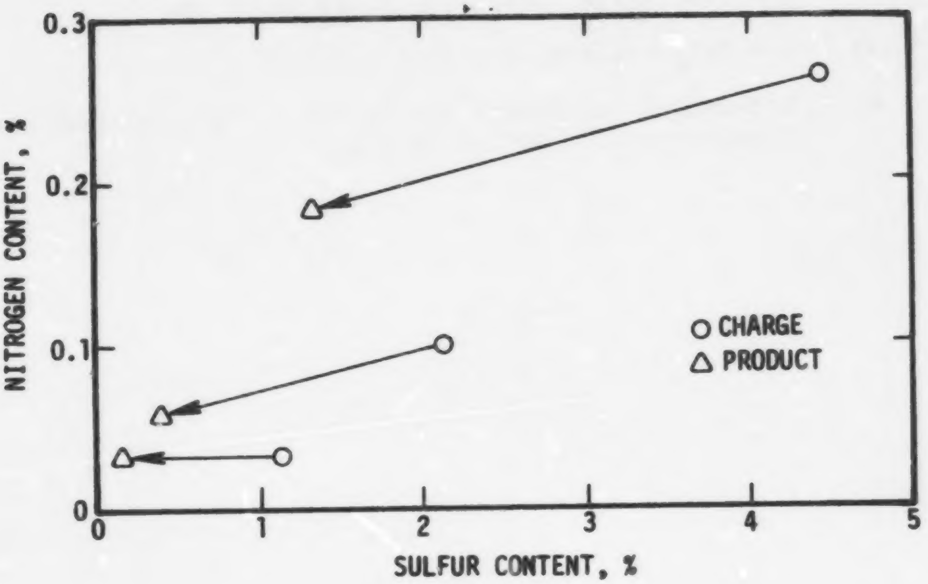


Figure 17. Reduction of nitrogen by hydrodesulfurization of heavy oil.

Research and development on the following may be required for further NO_x control in Japan:

1) Control techniques, such as fluidized bed combustion, for coal- or coke-fired processes.
2) Control techniques for high-temperature furnaces, such as those used for glass-melting.
3) Low-NO_x burners for LPG firing.
4) Effective catalysts for better nitrogen removal in hydrodesulfurization of fuel.

SECTION 3

DRY PROCESSES FOR NO_x REMOVAL

GENERAL DESCRIPTION

Classification of Dry Processes

Dry processes for denitrification that have been developed in Japan may be classified as follows:

1. Selective catalytic reduction (SCR) with ammonia
2. Ammonia reduction without catalyst
3. Activated carbon process (simultaneous removal of NO_x and SO_2)
4. Electron beam radiation (simultaneous removal of NO_x and SO_2)
5. Adsorption
6. Catalytic decomposition

SCR has been used commercially in many plants (Tables 8 and 9). Pilot-plant tests have been carried out with other processes.

Reduction of NO_x with Ammonia

Usual reactions of ammonia with NO_x are shown in equations (1) and (2).

$$4NH_3 + 6NO = 5N_2 + 6H_2O \tag{1}$$

$$8NH_3 + 6NO_2 = 7N_2 + 12H_2O \tag{2}$$

Table 8. MAJOR PLANTS USING DENITRIFICATION BY SELECTIVE CATALYTIC REDUCTION (SCR)

Process developer	Plant owner	Plant site	Capacity, Nm^3/hr	Source of gas	Completion
Sumitomo Chemical	Sumitomo Chemical	Sodegaura	30,000	Oil-fired boiler	July 1973
Sumitomo Chemical	Higashi Nihon Methanol	Sodegaura	200,000*	Heating furnace	May 1974
Sumitomo Chemical	Nihon Ammonia	Sodegaura	250,000*	Heating furnace	Mar. 1975
Sumitomo Chemical	Sumitomo Chemical	Anegasaki	100,000*	Gas-fired boiler	Feb. 1975
Sumitomo Chemical	Sumitomo Chemical	Anegasaki	200,000*	Gas-fired boiler	Feb. 1975
Sumitomo Chemical	Sumitomo Chemical	Niihama	200,000*	Heating furnace	Mar. 1975
Sumitomo Chemical	Sumitomo Chemical	Sodegaura	250,000	Oil-fired boiler	Mar. 1976
Sumitomo Chemical	Sumitomo Chemical	Sodegaura	300,000	Oil-fired boiler	Oct. 1976
Hitachi Shipbuilding	Kansai Oil	Sakai	5,000	Oil-fired boiler	Nov. 1973
Hitachi Shipbuilding	Idemitsu Kosan	Chiba	350,000	CO-fired boiler	Nov. 1975
Hitachi Shipbuilding	Shindaikyowa Pet. Chem.	Yokkaichi	440,000	Oil-fired boiler	Dec. 1975
Tokyo Electric-Mitsubishi H.I.	Tokyo Electric	Minamiyokahama	10,000*	Gas-fired boiler	Jan. 1974
Kurabo	Kurabo	Hirakata	5,000	Oil-fired boiler	Nov. 1973
Kurabo	Kurabo	Hirakata	30,000	Oil-fired boiler	Aug. 1975
Kansai Electric-Hitachi Ltd.	Kansai Electric	Sakaiminato	4,000	Oil-fired boiler	Jan. 1975
IHI-Mitsui Toatsu	Chubu Electric	Shinnagoya	8,000	Oil-fired boiler	Oct. 1974
Chubu-MKK	Chubu Electric	Yokkaichi	100	Oil-fired boiler	Oct. 1974
Mitsubishi H.I.	Mitsubishi H.I.	Hiroshima	4,000	Oil-fired boiler	Dec. 1974
Kobe Steel	Kobe Steel	Kakogawa	600	Sintering plant	May 1974
Mitsui Toatsu	Mitsui Toatsu	Sakai	1,000*	Gas-fired boiler	Oct. 1973
Mitsui Toatsu	Mitsui Toatsu	Sakai	3,000	Oil-fired boiler	Oct. 1974
Mitsui Toatsu	San Polymer	Osaka	4,000*	Gas-fired boiler	Oct. 1974
Mitsui Toatsu	Japan Novopan	Sakai	8,000*	Gas-fired boiler	June 1974
Hitachi Ltd.-Mitsubishi P.C.	Mitsubishis P.C.	Yokkaichi	150,000	Oil-fired boiler	Dec. 1975
Hitachi Ltd.	Kawasaki Steel	Chiba	350,000	Coke oven	Oct. 1976
Ube Industries	Chiba Pet. Chem.	Chiba	10,000	Oil-fired boiler	Jan. 1975
Mitsui S.B.-Mitsui P.C.	Mitsui Pet. Chem.	Chiba	200,000	Oil-fired boiler	Sept. 1975
Mitsui S.B.-Mitsui P.C.	Ukishima Pet. Chem.	Chiba	240,000	Oil-fired boiler	Aug. 1976
MKK-Santetsu	Okayama Paper	Okayama	1,500	Oil-fired boiler	Dec. 1974
MKK-Santetsu	Kawasaki Steel	Chiba	1,000	Coke oven	Mar. 1975
MKK-Santetsu	Nippon Yakin	Kawasaki	15,000	Oil-fired boiler	June 1976
Seitetsu Kagaku	Seitetsu Kagaku	Kakogawa	15,000	Oil-fired boiler	June 1975
Japan Gasoline	Kashima Oil	Kashima	50,000	Heating furnace	Nov. 1975
Japan Gasoline	Fuji Oil	Sodegaura	70,000	CO boiler	Mar. 1976
Asahi Glass	Asahi Glass	Keihin	70,000	Glass furnace	Apr. 1976

* Clean gas; those without asterisks are for dirty gas.

Table 9. DENITRIFICATION PLANTS PLANNED BY COMPANIES

Company	Plant site	Capacity, MW	Fuel	Process	Scheduled completion
Hokkaido Elec.	Tomakomai	300	Coal	N.d.*	1978
Chubu Elec.	Chita	700 x 2	LNG	SCR †	1977
Kyushu Elec.	Kokura	600 x 2	LNG	SCR ‡	1978-79
EPDC	Isogo	265 x 2	Coal	AR§	1977-78
EPDC	Takasago	250 x 2	Coal	AR§	1977-78
Tobata Kyodo	Tobata	375	LNG	N.d. †	1980
Chubu Elec.	Chita	375	Oil	AR§	1977

* Not determined

† SCR (Hitachi, Ltd.)

‡ SCR (Mitsubishi Heavy Industries)

§ Ammonia reduction, possibly by the Exxon Process

Since the presence of oxygen promotes the reactions, the actual reactions may be better represented by equations (3) and (4).

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O \quad (3)$$

$$4NH_3 + 2NO_2 + O_2 = 3N_2 + 6H_2O \quad (4)$$

In addition, the following reactions between ammonia and oxygen can take place:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad (5)$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad (6)$$

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \quad (7)$$

Virtually all of the NO_x in a combustion gas is present as NO. The optimum temperature for reaction of NO and NH_3 (equation 3) without a catalyst is in a narrow range at about 1000°C. The reaction rate is low below this temperature, whereas an undesirable reaction (equation 6) predominates at higher temperatures. Use of a catalyst lowers the reaction temperature to 300° to 450°C and prevents the undesirable reaction.

Problems of Ammonia Reduction Processes

The major problem with a catalyst is that it becomes plugged with dust in the flue gas. Dust from oil burning (Table 10) does not poison the catalyst seriously but tends to cover the catalyst surface, resulting in lower reactivity and a greater pressure drop. Several devices have been developed to minimize the influence of dust. For example, a parallel-passage reactor has been used commercially, and moving-bed reactors have been tested in pilot plants.

Table 10. COMPOSITION OF DUST FROM OIL BURNING (12)
(%)

	C	SiO_2	SO_4	V_2O_5	$Fe_2O_3\cdot$	$\cdot Al_2O_3$	NiO	CaO	MgO	Na_2O
A	9.8	6.0	42.6	18.0	4.6	5.3	2.3	5.7	1.8	11.9
B	5.9	2.4	58.4	12.2	3.6	1.5	2.6	3.0	2.5	14.8

Another problem is catalyst poisoning by SO_x in exhausts from boilers burning coal and oil and by alkaline vapor in exhausts from glass-melting furnaces, cement kilns, and other sources. SO_x mainly affects the catalyst carrier, which is usually porous alumina. Alumina tends to react with SO_x, particularly with SO_3, to form aluminum sulfate, leading to a decrease in surface area and catalyst activity (Figure 18). Titania and silica are more resistant to SO_3 than alumina.

Base metal oxides commonly used as catalysts also tend to react with SO_x to form sulfates. The sulfates, however, are usually still reactive and less likely to promote the decomposition of ammonia by reacting with oxygen. Therefore, some catalysts are made of base metal sulfates.

A serious problem common to ammonia reduction processes with or without catalyst is the formation of ammonium

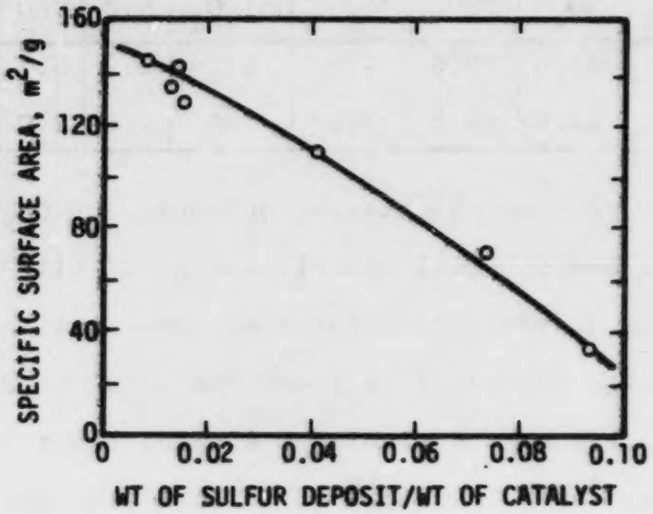


Figure 18. Deactivation of catalyst on γ-Al_2O_3 carrier by SO_x.[1]

bisulfate, as shown in Figure 19. For example, when the gas contains 10 ppm each of SO_3 and NH_3, liquid ammonium bisulfate forms at 210°C. The bisulfite usually is formed in a heat exchanger used for heat recovery after the reduction. The bisulfite melt is corrosive, and it disturbs the heat transfer. At lower temperatures, the bisulfate solidifies and often reacts with ammonia to form ammonium sulfate. A corrosion-resistant material must be used for the heat exchanger. During plant operation, it is necessary to remove the bisulfate or sulfate from the exchanger occasionally by steam blowing or water washing.

MHI SCR PROCESSES (13)

Clean Gas Treatment

Since 1973 Mitsubishi Heavy Industries (MHI) has tested SCR in a laboratory and at a pilot plant with a capacity of treating 100,000 Nm^3/hr of flue gas from an LNG-fired boiler at Minamiyokohama Station, Tokyo Electric.

Granular base-metal catalysts with an alumina carrier (2 to 4 mm in diameter) have been used. Figure 20 shows results of laboratory tests with various catalysts at temperatures between 150° and 500°C and their effect on the denitrification ratio and NH_3 concentration in the outlet gas. Catalysts made of Cr_2O_3 and Pt were reactive at low temperatures (200° to 220°C) but showed a tendency to con-

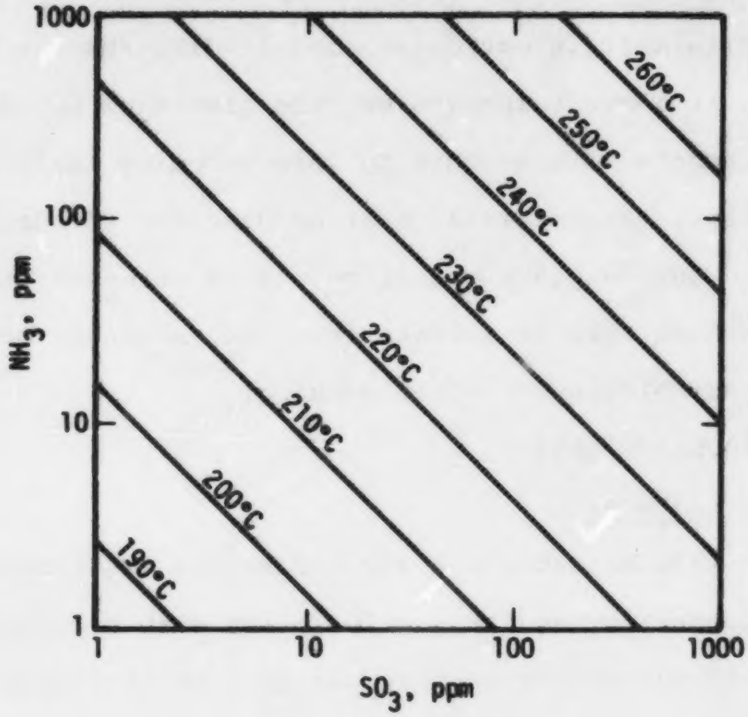


Figure 19. Formation temperature of NH_4HSO_4.

$$\left(\underset{\text{Gas}}{NH_3} + \underset{\text{Gas}}{SO_3} + \underset{\text{Gas}}{H_2O} \rightleftarrows \underset{\text{Liquid}}{NH_4HSO_4}\right)$$

vert a portion of NH_3 into NO at higher temperatures. Catalysts made of Cr_2O_3 with other oxides yielded good results.

Figure 21 shows results of a 5500-hour life test of a selected catalyst. The effect of O_2 concentration on denitrification is presented in Figure 22. These results indicate that when more than about 1 percent O_2 is present in the gas, 90 percent denitrification is achieved at 320° to 450°C with a space velocity of 10,000 hr^{-1} and an NH_3/NO_x mole ratio of 1. Unreacted ammonia in the outlet gas is kept at 10 ppm or below. The catalyst has shown no tendency to decrease in activity during the 5500-hour continuous test.

At one pilot plant, flue gas at 270° to 370°C could be obtained from a boiler either before or after the economizer (Figure 23). The NO_x concentration fluctuated between 50 and 130 ppm with the boiler load. Figure 24 shows the effect of boiler load on NO_x removal ratio and NH_3 concentration of the outlet gas. When the load was reduced, the temperature fell. The NO_x removal rate did not decrease, however, because the space velocity decreased and O_2 concentration increased.

At the pilot plant, tests were made to reduce ammonia emissions by using an additional converter with an ammonia decomposition catalyst. The effect of the converter is

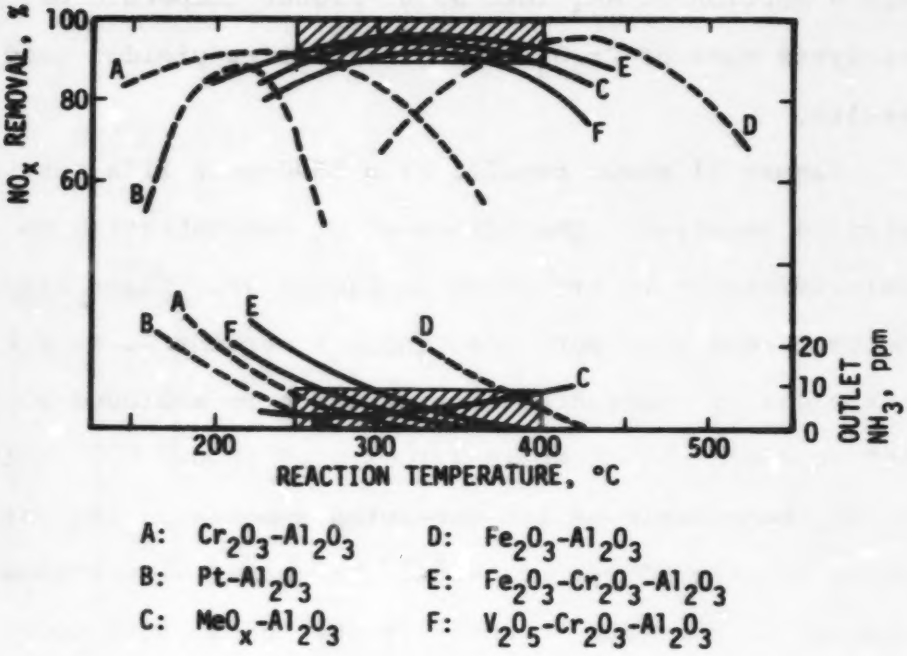


Figure 20. Criteria for catalyst for clean gas.

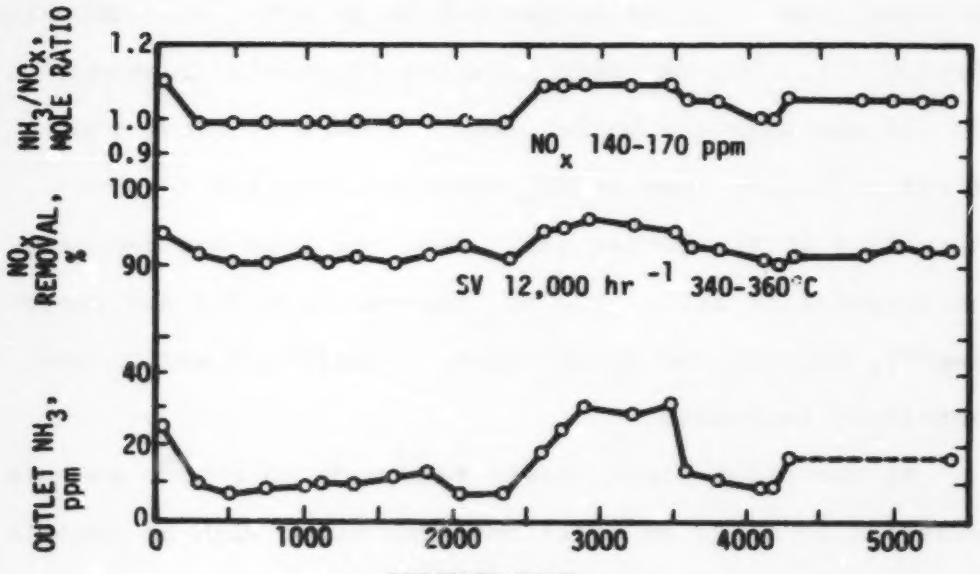


Figure 21. Durability of catalyst for clean gas.

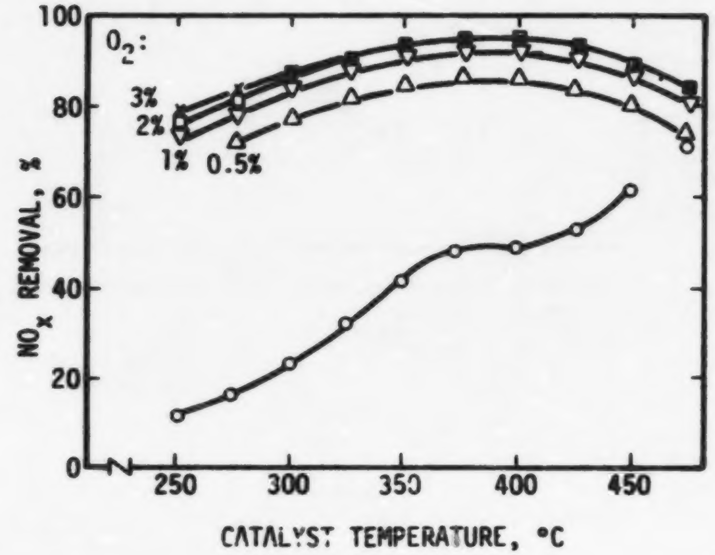


Figure 22. Effect of oxygen on NO_x removal.

(SV, 10,000 hr^{-1}; NO_x, 100 ppm; NH_3/NO_x, 1.0)

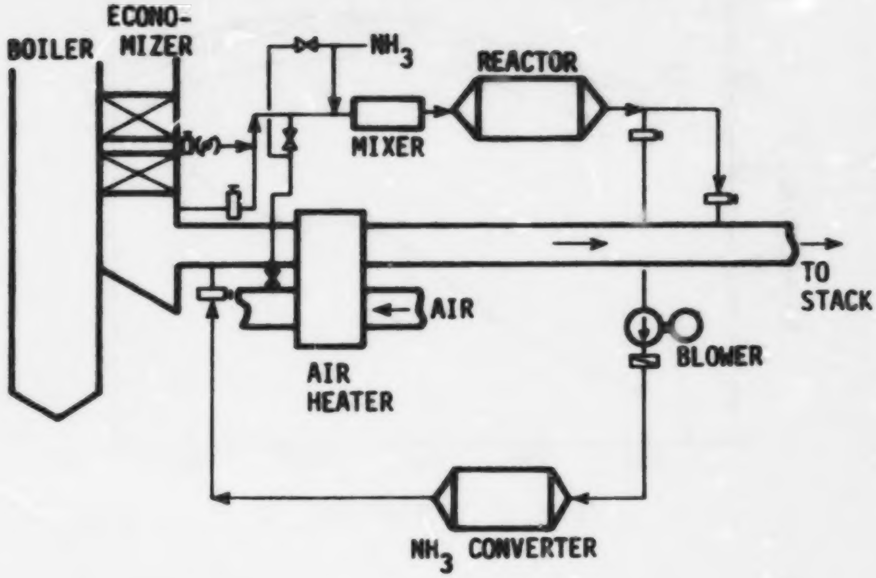

BOILER
ECONO-
MIZER
NH3
REACTOR
MIXER
AIR
TO
STACK
BLOWER
AIR
HEATER
NH3 CONVERTER

Figure 23. Flowsheet of pilot plant (clean gas).

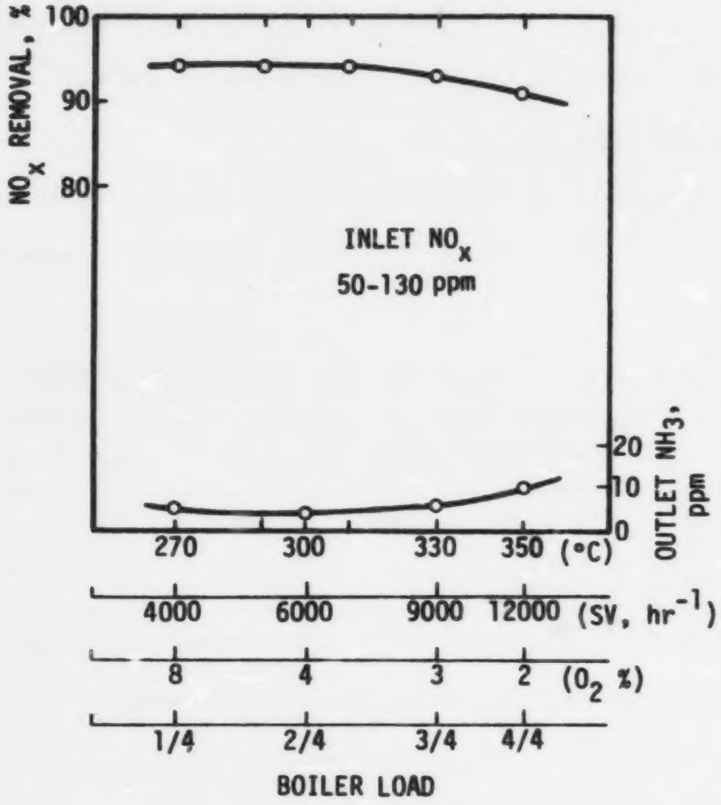


Figure 24. Effects of boiler load on NO$_x$ removal.

shown in Figure 25. Ammonia in the treated gas was reduced to 1 or 2 ppm, and the denitrification efficiency was increased to about 97 percent.

MHI recently obtained an order from Kyushu Electric for construction of large commercial SCR plants for two LNG boilers (600 MW each) to be completed in 1978.

Dirty-Gas Treatment

MHI has made tests with dirty flue gas from low-sulfur oil burning. Examples of the gas composition are shown in Table 11.

Table 11. EXAMPLES OF GAS COMPOSITION

	O_2, %	NO_x, ppm	SO_2, ppm	SO_3, ppm	Dust, mg/Nm^3
Full load	1.0	160	80	3	20
25% load	3.0	80	60	2	15

Screening tests were made on several catalysts. The SO_3 resistivity of the catalyst carrier was as follows:

$$TiO_2 = SiO_2 > \alpha\ Al_2O_3 > \eta\ Al_2O_3 > \gamma\ Al_2O_3$$

Metals used for the catalyst were Cu, V, Cr, Mn, Fe, Co, and Ni. These were tested alone and in combination. Selected catalysts have been tested further.

Bench-scale tests with catalysts in a fixed bed have shown that a spherical catalyst 3 millimeters in diameter causes serious dust plugging whereas a catalyst 8 millimeters

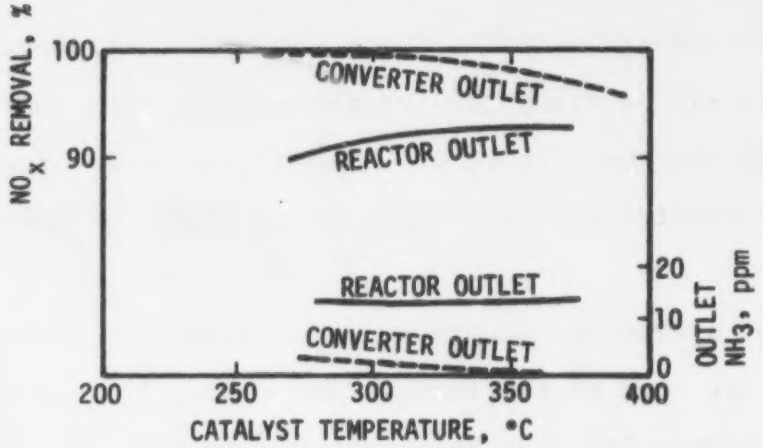


Figure 25. Effects of ammonia converter.

(Gas flow, 12,000 Nm^3/hr; NH$_3$/NO$_x$, 1.0; NO$_x$, 150 ppm) in diameter does not (Figure 26). The larger catalyst, however, gives poor denitrification efficiency (Figure 27). Therefore, a catalyst 4 to 6 millimeters in diameter has been used in later tests.

Tests have been carried out at a pilot plant with capacity for treating 4000 Nm^3/hr of flue gas from the burning of low-sulfur oil. The pilot plant includes two units, one with a fixed-bed reactor and the other with a moving-bed reactor (Figure 28). Both have an air heater after the reactor to allow tests of formation of ammonium bisulfate.

A hot electrostatic precipitator (ESP) was installed and used for most of the tests. The shape of the reactor is shown in Figure 29. The catalyst is placed in a W-shaped container developed by MHI. The container allows a uniform gas flow at a low pressure drop, and the catalyst can be replaced easily. The catalyst layer is 100 to 200 millimeters thick.

The relationship of gas temperature and space velocity to denitrification ratio when the fixed bed was used with the ESP is shown in Figure 30. About 90 percent removal was obtained at 360°C, with a space velocity of 10,000 hr^{-1}, and with an NH_3/NO_x mole ratio of 1. The NH_3 content of the reactor effluent was below 15 ppm (Figure 31). Results of a

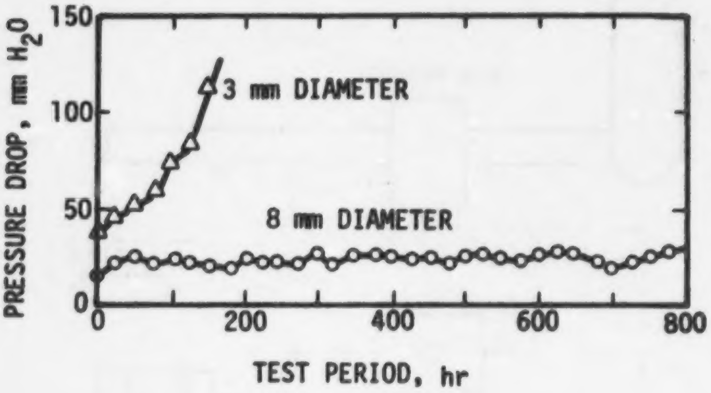


Figure 26. Pressure drop in fired-bed reactor with different catalyst diameters. (Dust 10-20 mg/Nm^3)

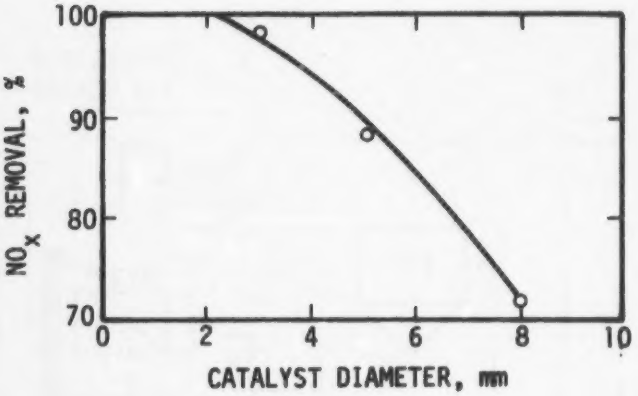


Figure 27. Effect of catalyst size on NO_x removal. (SV, 10,000 hr^{-1}, Temp, 360-370°C, NH_3/NO_x, 1.0)

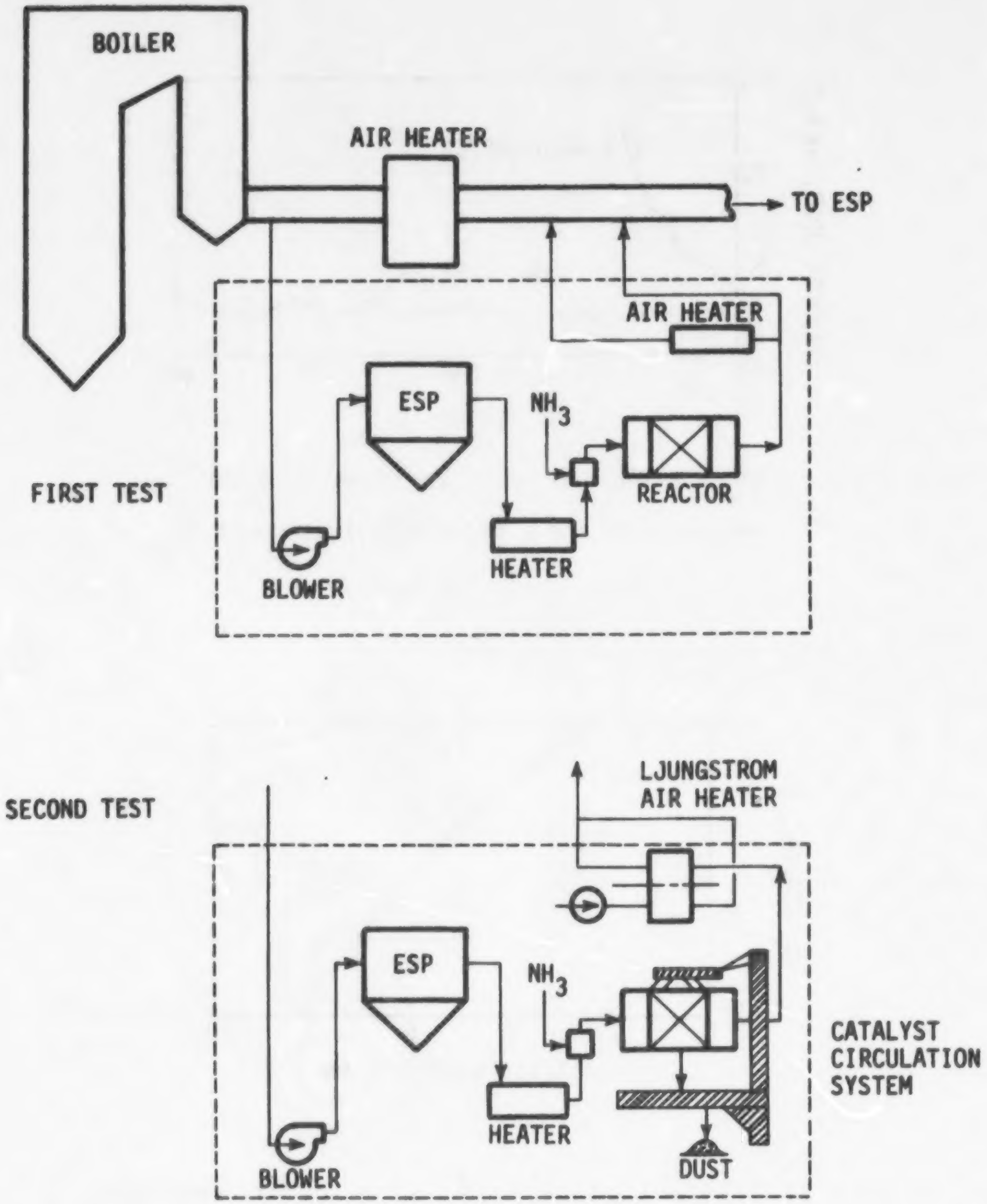

BOILER
AIR HEATER
TO ESP
AIR HEATER
ESP
NH_3
REACTOR
FIRST TEST
HEATER
BLOWER
SECOND TEST
LJUNGSTROM
AIR HEATER
ESP
NH_3
CATALYST
CIRCULATION
SYSTEM
HEATER
BLOWER
DUST

Figure 28. Systems of pilot plant tests.

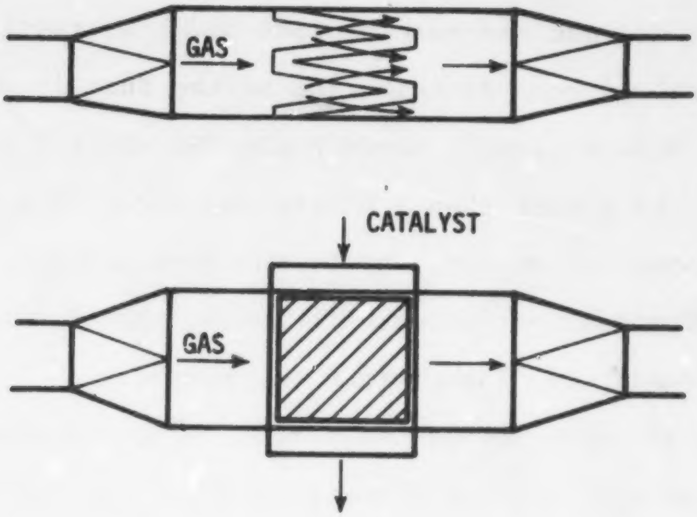

GAS
CATALYST
GAS

Figure 29. Structure of moving-bed reactor.

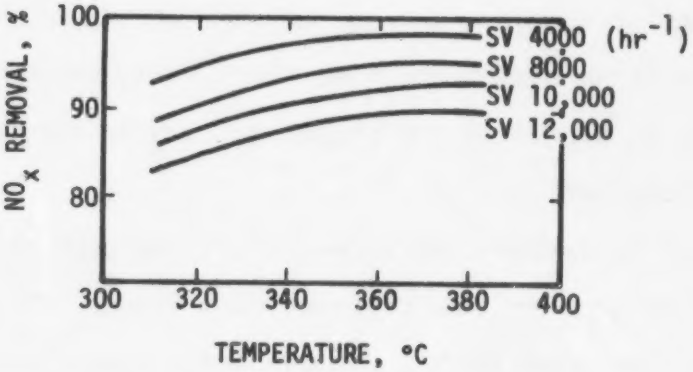


Figure 30. Results of first test.

(Fixed bed; NH_3/NO_x = 1.0)

catalyst life test are shown in Figure 32. The activity of the catalyst did not decrease in 1500 hours of testing.

The particle size distribution of the dust is shown in Figure 33. Before passing through the ESP about 5 percent of the dust was larger than 1 micron and about 20 percent was larger than 0.2 micron. After the precipitator, 2 to 3 percent of the dust particles were larger than 1 micron and about 10 percent were larger than 0.2 micron.

Figure 34 shows results of a test using a moving bed (with intermittent moving) without an ESP. Pressure drop increased at a rate of 7.3 to 13.4 millimeters per day. When it reached 160 millimeters H_2O, the bed was moved to replace 10 to 20 percent of the catalyst. The pressure drop then was reduced to 60 millimeters H_2O. This test indicates that by use of a moving bed an ESP may be eliminated. When the gas contains much more dust, some dust-removal equipment, such as an ESP or multicyclone, may be needed even with a moving bed.

Figure 35 depicts measurements of deposit of ammonium bisulfate on the air heater (heat exchanger). The maximum deposit occurred at 200°C, in agreement with Figure 19. The deposits must be removed by some means.

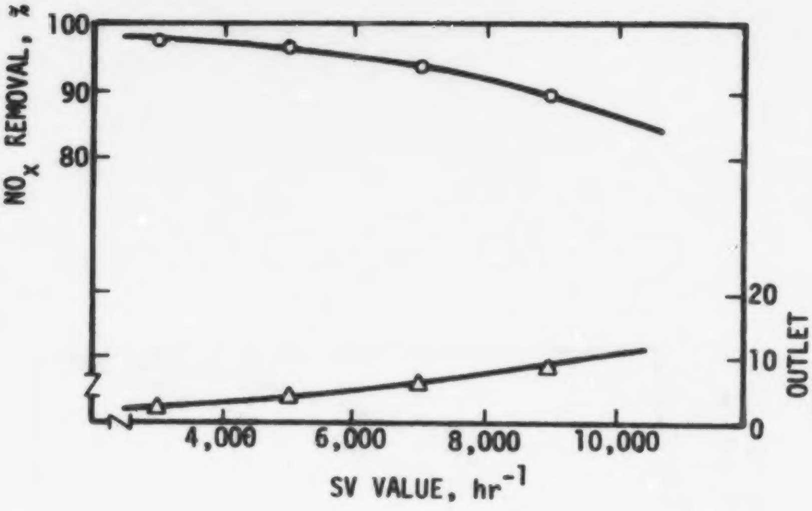


Figure 31. Effect of SV on NO_x removal and NH_3 emission

(Catalyst diameter, 4-6 mm; inlet NO_x, 150 ppm; Temperature, 380°C; $NH_3/NO_x = 1.0$).

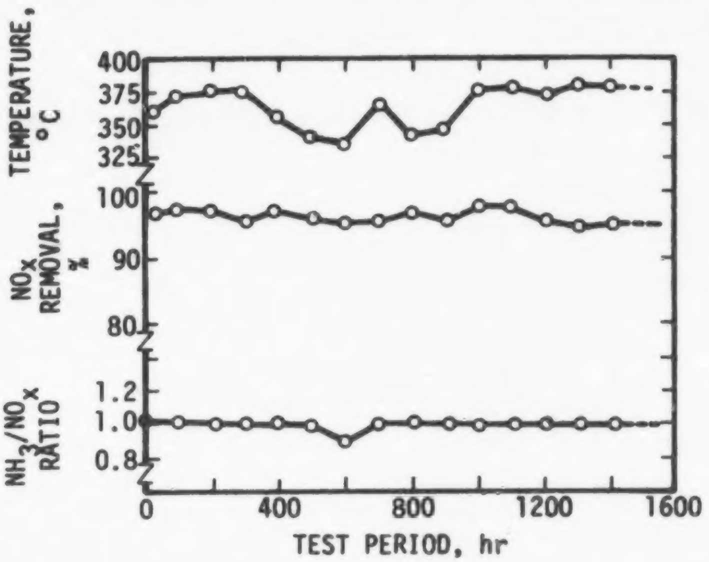


Figure 32. Durability of NO_x reduction catalyst for low-sulfur oil-burning gas.

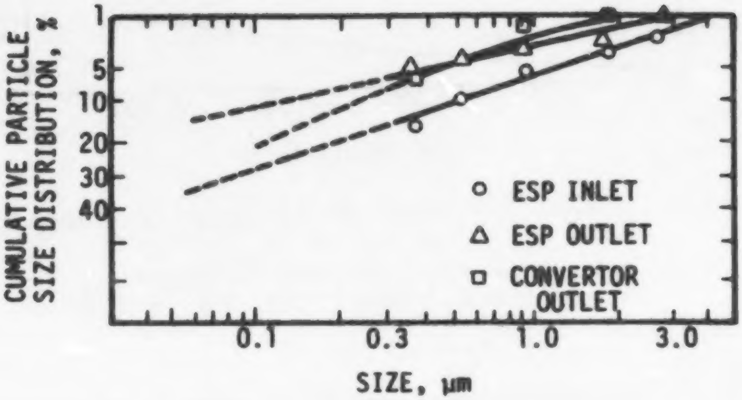


Figure 33. Particle size distribution of dust.

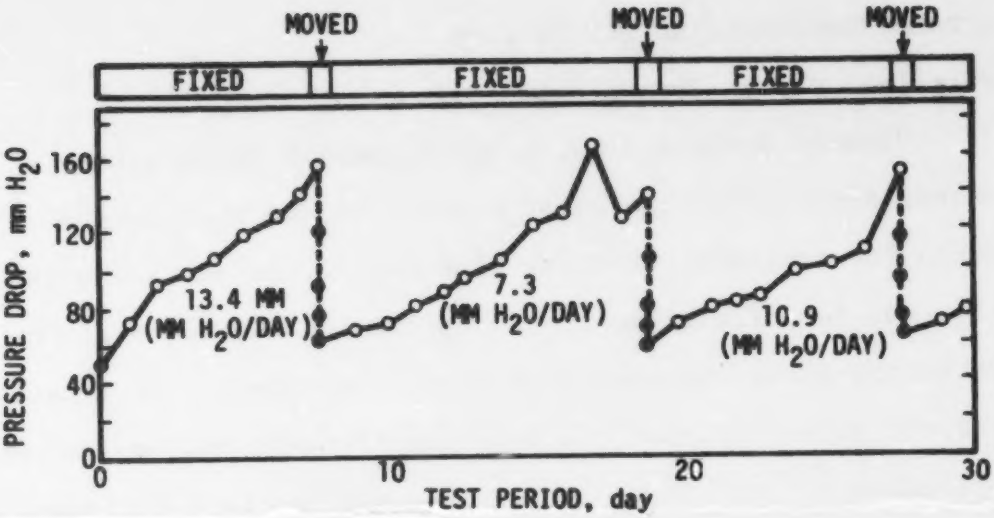


Figure 34. Change of pressure drop with moving bed.

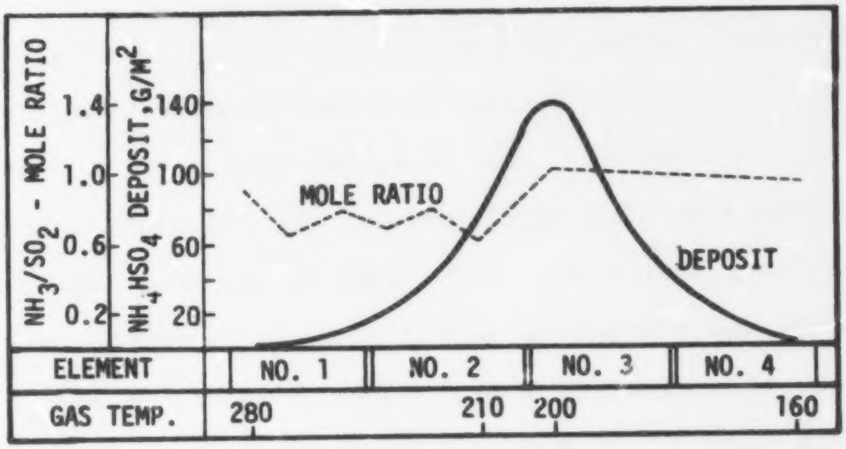


Figure 35. Deposit of NH_4HSO_4 in air heater.

HITACHI SHIPBUILDING SCR PROCESS

Yokkaichi Plant, Shindaikyowa Oil

Hitachi Shipbuilding, after extensive pilot plant tests, constructed the first commercial SCR unit in the world for treatment of dirty flue gas in conjunction with flue gas desulfurization. The unit was constructed at the Yokkaichi plant, Shindaikyowa Oil, with capacity of treating 440,000 Nm^3/hr of flue gas from an oil-fired boiler (140 MW equivalent). The flue gas is first treated by a Wellman-Lord process plant constructed by Mitsubishi Kakoki Kaisha (MKK) to reduce SO_2 from 1500 to 100 ppm and dust from 140 to 40 mg/Nm^3. The by-product of the flue gas desulfurization plant is sulfuric acid, which is consumed at the Yokkaichi plant.

A flowsheet of the denitrification system is shown in Figure 36. At about 55°C, gas from the scrubber contains 150 ppm NO_x, 150 ppm SO_2, and 40 mg/Nm^3 dust. It is heated in Ljungstrom-type heat exchangers to 310° to 320°C and then in an auxiliary heater to 420°C. The gas is then injected with ammonia and introduced into a reactor specially designed to minimize the effect of dust. Space velocity in the catalyst is 5,000 to 10,000 hr^{-1}, and the NH_3/NO_x ratio, about 1.2. The NO_x concentration after the reactor is 30 to 40 ppm (75 to 80 percent removal); concentration after the

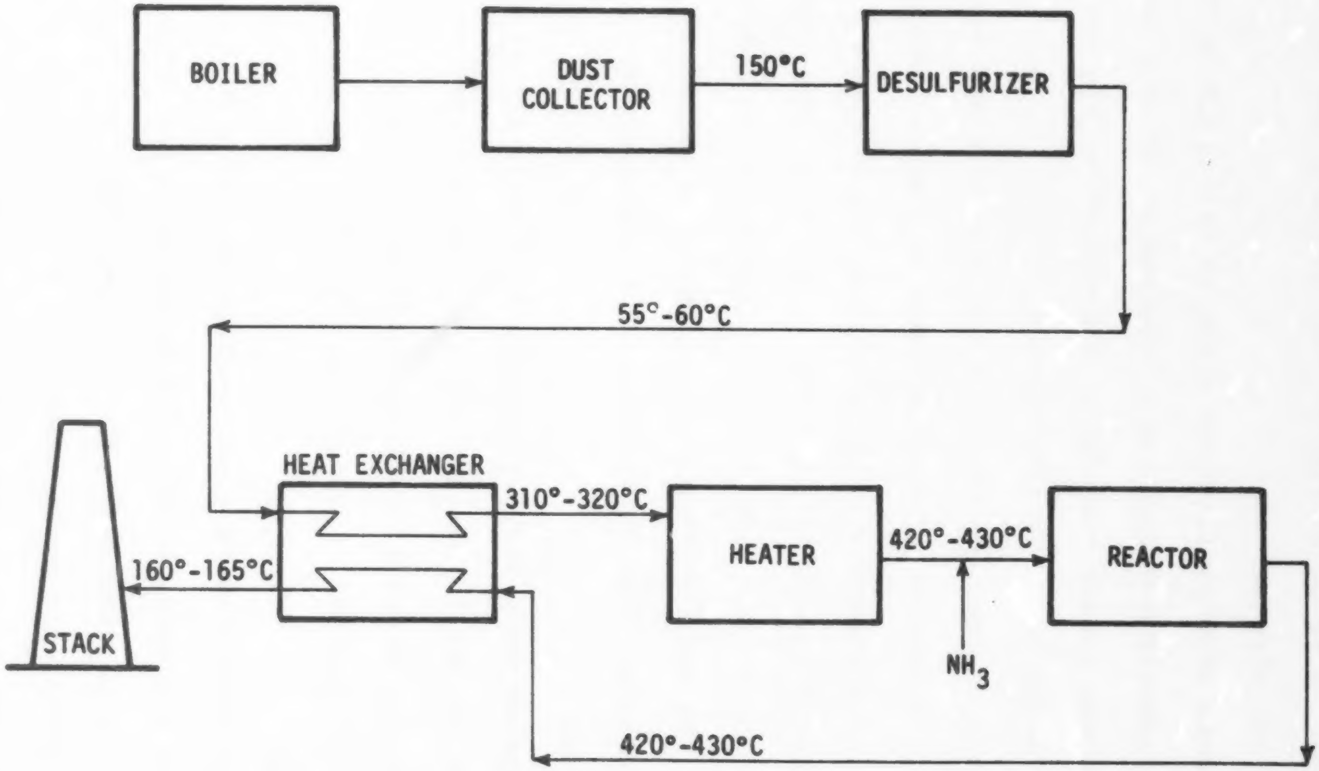

BOILER
DUST COLLECTOR
150°C
DESULFURIZER
55°-60°C
HEAT EXCHANGER
310°-320°C
HEATER
420°-430°C
NH_3
REACTOR
420°-430°C
160°-165°C
STACK

Figure 36. Flowsheet of Hitachi Shipbuilding process (an example of dirty-gas treatment).

heat exchanger is 40 to 50 ppm because of inlet gas leaking into the outlet stream.

No ammonia decomposition catalyst is installed in the system, but ammonia emissions are reported to be very low, possibly because excess ammonia is decomposed at the relatively high temperature in the reactor.

The plant started operation in January 1976 and has since been in operation without serious problems. Temperature of the heat exchanger effluent gas is about 160°C. Because ammonium bisulfate deposits in the heat exchanger, soot blowers have been used several times a day to remove bisulfate. The heat exchanger is coated with enamel to prevent corrosion. The catalyst life is expected to be about one year.

The capital cost was $20 million ($143/kW) for flue gas desulfurization and $7 million ($50/kW) for denitrification. In addition, the company spent $3 million for miscellaneous items for both systems.

Other Plants

Hitachi Shipbuilding also constructed for Idemitsu Kosan, at its Chiba refinery, a unit with a capacity for treating 350,000 Nm^3/hr of flue gas. The flue gas from the refinery, containing relatively small amounts of SO_2 and dust, is subjected to denitrification without desulfurization. The denitrification system, similar to that of Shindaikyowa Oil, has been in operation since November 1975.

Hitachi Shipbuilding is to construct a plant for Kawasaki Steel at its Chiba Works to treat 840,000 Nm^3/hr of flue gas from an iron-ore sintering plant. The gas contains not only 300 to 500 ppm SO_2 and a considerable amount of dust, but also a small amount of an alkaline vapor that contaminates the catalyst. The gas passing through an ESP will be treated first by lime scrubbing, then by a wet ESP to clean the gas, and finally by a denitrification system.

The Cement Producers Association has been operating a pilot plant constructed by Hitachi Shipbuilding with a capacity of treating 5000 Nm^3/hr of flue gas from a cement kiln at the Nanyo Plant, Tokuyama Soda. The gas, with a low SO_2 concentration but high dust content, is passed through an ESP and then treated by the denitrification unit. Dust plugging has been a problem, and Hitachi Shipbuilding is to change the reactor design and catalyst shape.

Hitachi Shipbuilding has been operating several small test units (150 to 250 Nm^3/hr) for SCR with flue gas from a coal-fired boiler at Isogo Station, Electric Power Development Company. The gas from an economizer of the boiler at about 400°C, containing about 15 g/Nm^3 dust, 300 ppm SO_2, and 250 ppm NO_x, is treated without dust removal. Details of operation and efficiency have not been reported.

Economics

Hitachi Shipbuilding reports that the capital cost (battery limits) for a denitrification plant similar to that of Shindaikyowa Oil is about \$6.7 million. The 300,000 Nm^3/hr plant is equivalent to 100 MW, and the cost includes the heat exchanger. The cost of removing about 85 percent of the NO_x from a 150-ppm gas stream, is estimated at \$15 per kiloliter of oil (3.3 mills/kWh), based on the following assumptions:

Annualization of fixed cost: 21% of total capital cost

8000 annual operating hours

Power: 3.3¢/kWh

Fuel: \$83/t

Steam: \$7/t

Ammonia: \$233/t

Catalyst: \$7500/m^3

1 year catalyst life

The cost would be higher for the Kawasaki Steel plant, which will have a wet electrostatic precipitator in addition to the above system. Kawasaki Steel is required to construct the plant under an agreement with the Chiba prefectural government.

HITACHI, LTD., SCR PROCESS

Hitachi, Limited, has tested SCR at several pilot plants with capacities to treat 200 to 4000 Nm^3/hr of flue gas from oil- and LNG-fired boilers and a coke oven. Various types of reactors with fixed and moving beds have been tested. Hitachi applied for a patent on base-metal catalysts that are deposited on alumina on the same day that Exxon applied for a similar patent.

Some results of the pilot plant tests are shown in Figures 37 and 38. More than 90 percent of the NO_x is reacted with ammonia at 380° to 400°C, and more than 80 percent is reacted at about 300°C, using an NH_3/NO_x mole ratio of 0.9 to 1.0 and a space velocity of 10,000 to 20,000 hr^{-1}. The ammonia concentration in the reactor effluent gas is about 2 ppm at a space velocity of 10,000 hr^{-1} and about 5 ppm at a space velocity of 20,000 hr^{-1}.

In a joint venture with Mitsubishi Petrochemical, Hitachi developed a catalyst based on a titanate, which is more resistant to SO_x than alumina, and constructed a commercial plant (150,000 Nm^3/hr) (Table 8).

Hitachi is now constructing a larger commercial plant with a capacity to treat 500,000 Nm^3/hr of flue gas from coke ovens. Two reactors are used in parallel at the Chiba plant, Kawatetsu Chemical, a subsidiary company of Kawasaki Steel (Figure 39). Recently Hitachi received an order from Chubu Electric Power to construct SCR plants for two 700-MW LNG-fired boilers to be constructed at the Chiba Station by the end of 1977.

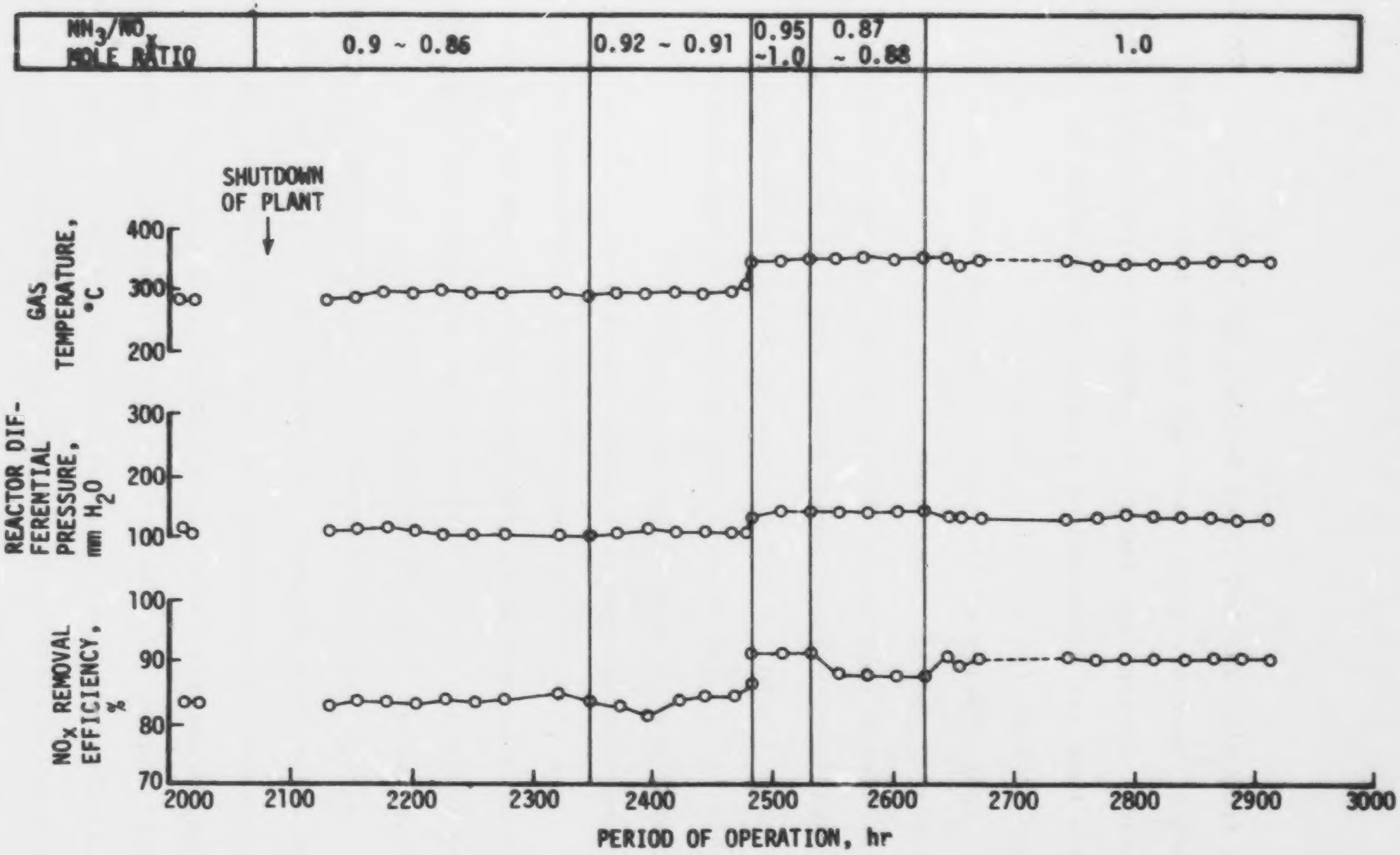


Figure 37. Hitachi SCR pilot plant test (LNG) at a space velocity of 20,000 hr^{-1}

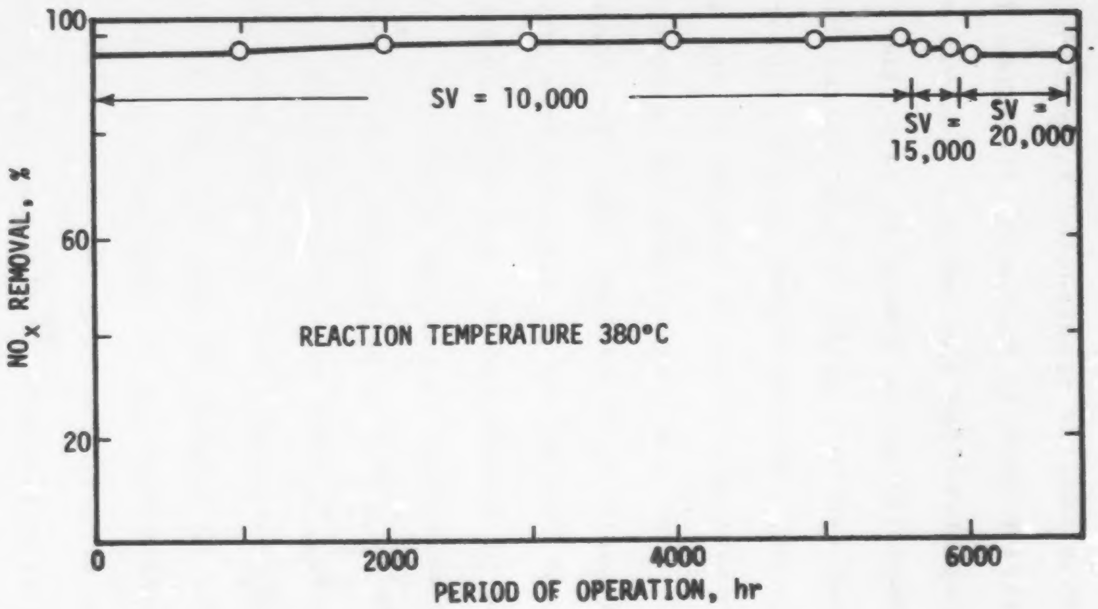


Figure 38. Hitachi SCR pilot plant tests after desulfurization (heavy oil).

JAPAN GASOLINE PARANOX PROCESS

Japan Gasoline Company, an engineering and plant construction firm that earlier constructed a Shell-process flue gas desulfurization unit at Yokkaichi for Showa Yokkaichi Sekiyu Co. (SYS), has developed its own SCR catalyst and has constructed two commercial units (Table 8) using the Shell-type parallel-passage reactor, which is less vulnerable to dust than other designs. The structure of the reactor and a flowsheet of the process are shown in Figures 40 and 41.

The first commercial plant was completed in November 1975 at the Kashima Refinery of Kashima Oil. The plant has a capacity to treat 50,000 Nm^3/hr of flue gas from the refinery (containing 60 to 250 ppm NO_x and about 50 mg/Nm^3 dust) and to remove more than 95 percent of the NO_x. Flue gas entering at 200° to 350°C is heated via a heat exchanger and an auxiliary heater to 390° to 420°C, injected with ammonia at an NH_3/NO_x ratio of 1.1/1.3, and introduced into the reactor. Figures 42 through 44 show the denitrification efficiency, NO_x concentration at the reactor inlet and outlet, and pressure drop in the reactor.

Very high removal efficiency is obtained with a relatively high pressure drop and a relatively low space velocity. The ammonia concentration of the reactor effluent is less than 10 ppm. There has been no problem of dust plugging

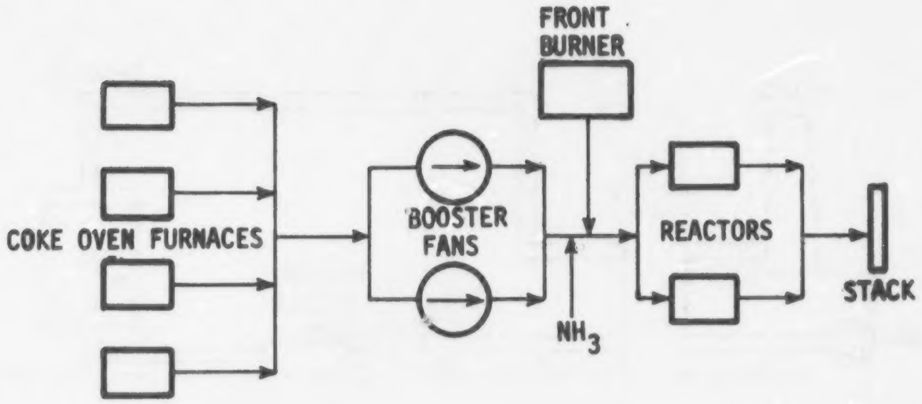

FRONT BURNER
COKE OVEN FURNACES
BOOSTER FANS
NH3
REACTORS
STACK

Figure 39. Flowsheet of Chiba plant, Kawatetsu Chemical.

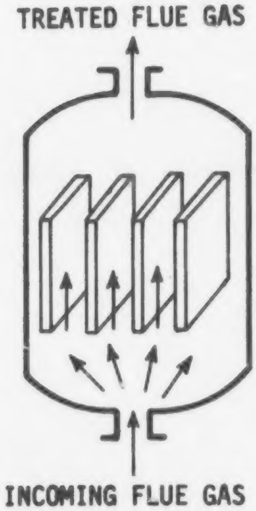

TREATED FLUE GAS
INCOMING FLUE GAS

Figure 40. Structure of parallel-passage reactor.

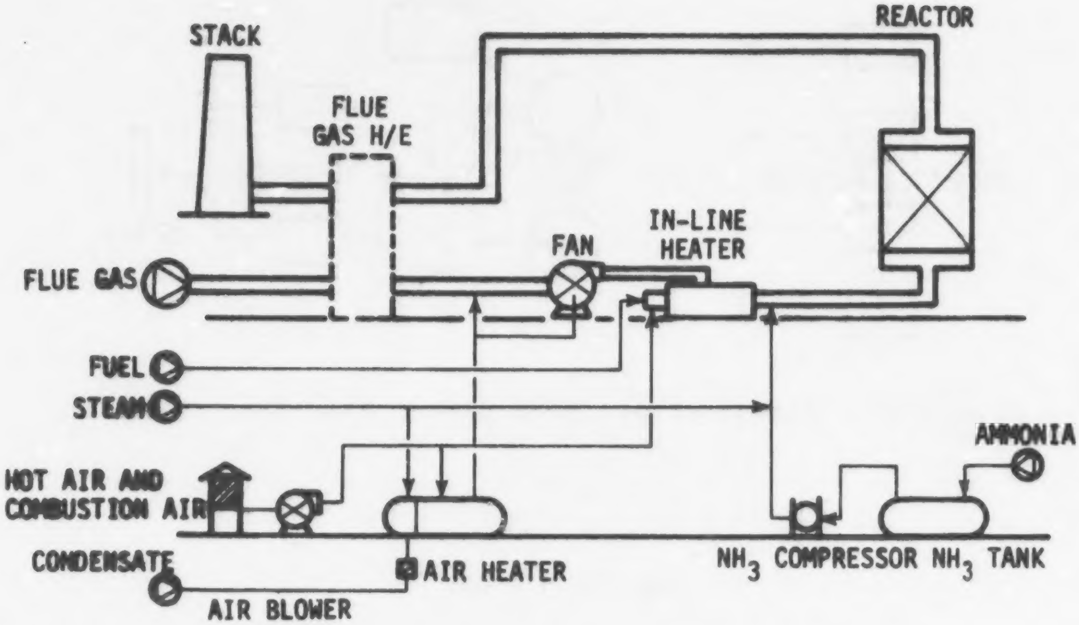

STACK
REACTOR
FLUE GAS H/E
IN-LINE HEATER
FAN
FLUE GAS
FUEL
STEAM
AMMONIA
HOT AIR AND COMBUSTION AIR
CONDENSATE
AIR HEATER
AIR BLOWER
NH_3 COMPRESSOR
NH_3 TANK

Figure 41. Flowsheet of Paranox process.

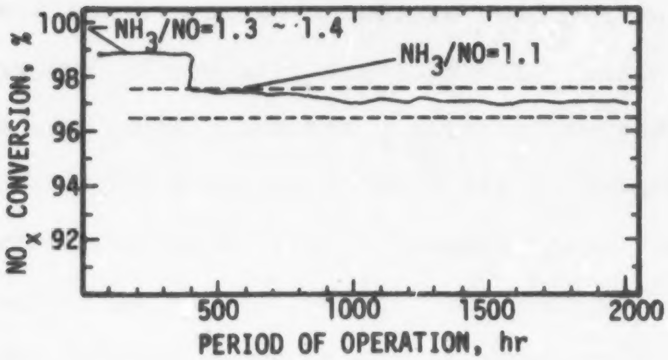


Figure 42. NO$_x$ removal ratio (Kashima plant).

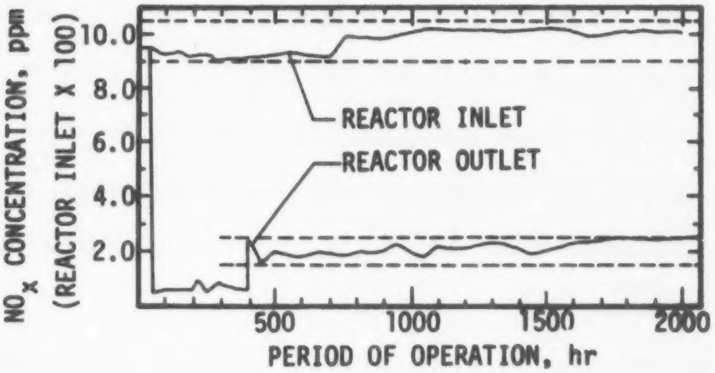


Figure 43. NO$_x$ concentration (Kashima plant).

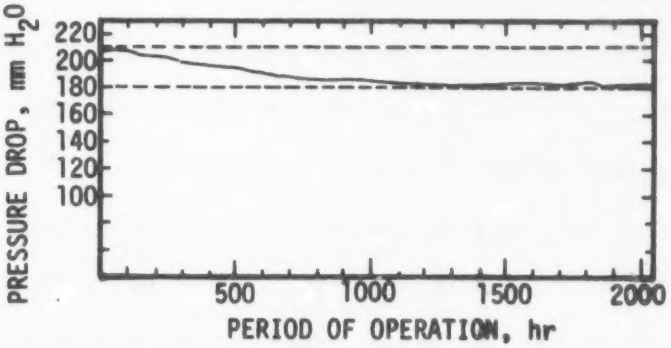


Figure 44. Pressure drop in reactor (Kashima plant).

during about 6 months of continuous operation since start-up of the plant. The catalyst life may be longer than the one year that was initially assumed. When less than 90 percent removal is sufficient, a higher space velocity may be used at a lower pressure drop. A recent estimate by Japan Gasoline puts the capital cost at $1.33 million for a 150,000 Nm^3/hr system giving 85 to 90 percent removal.

KURABO SCR PROCESS (14)

Kurabo has been testing an SCR process at a pilot plant with a capacity of treating 30,000 Nm^3/hr of flue gas from a boiler burning a high-sulfur oil. The plant uses moving beds to treat gas containing a high concentration of SO_2 and a considerable amount of dust. A flowsheet of the process is shown in Figure 45.

The reactor has three elements (Figure 46), each with capacity of treating 10,000 Nm^3/hr of gas. In each element the spherical catalyst, 5 millimeters in diameter, moves continuously downward. The gas passes horizontally through the elements. The catalyst bed is thin, and the gas velocity through the catalyst is relatively low to maintain the pressure drop in the reactor below 100 millimeters of H_2O.

A space velocity of 7000 to 10,000 hr^{-1} is normally used. The flue gas contains about 1600 ppm SO_2, 280 ppm NO_x, and nearly 100 mg/Nm^3 dust. More than 90 percent of the NO_x and more than 80 percent of the dust are removed in

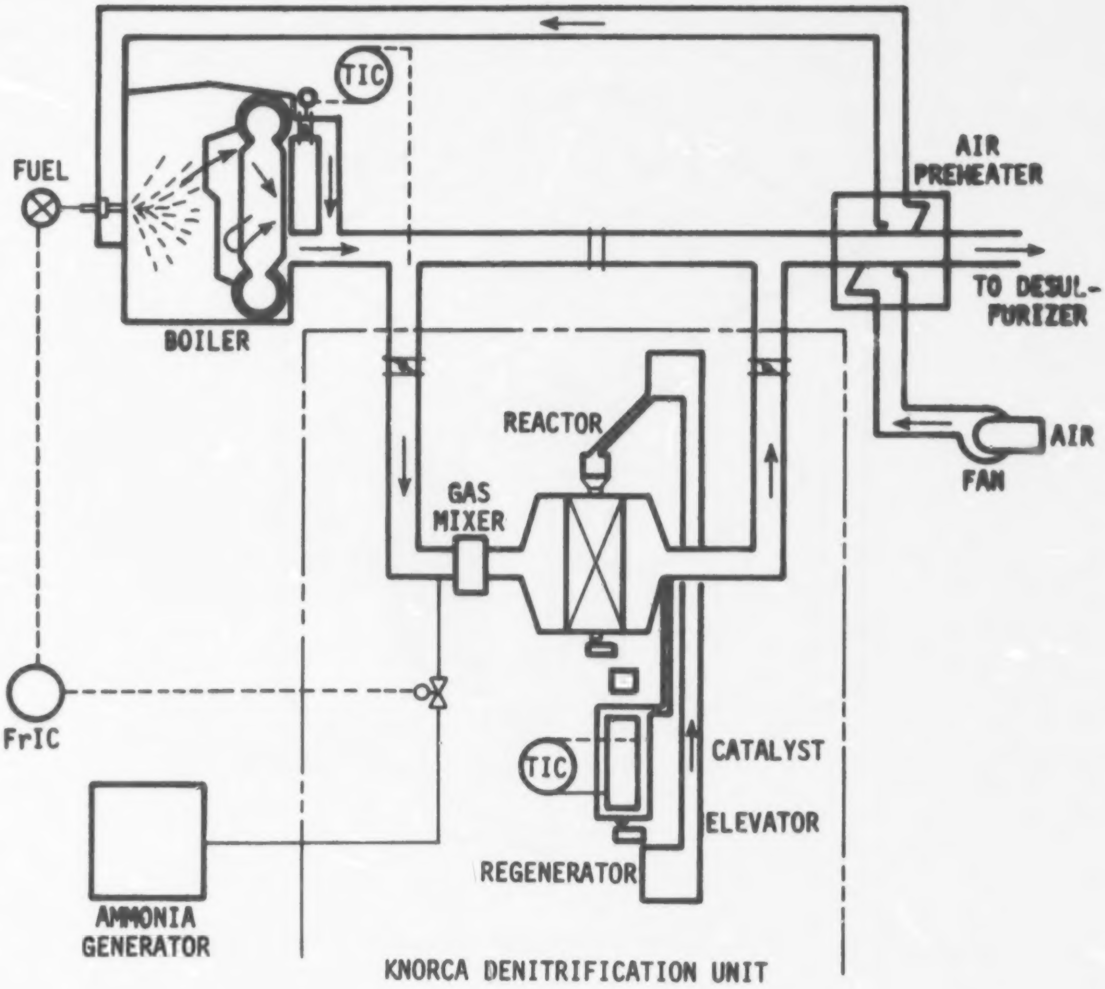

TIC
FUEL
AIR
PREHEATER
TO DESUL-
FURIZER
BOILER
REACTOR
AIR
FAN
GAS
MIXER
FrIC
TIC
CATALYST
ELEVATOR
REGENERATOR
AMMONIA
GENERATOR
KNORCA DENITRIFICATION UNIT

Figure 45. Flowsheet of Kurabo SCR process.

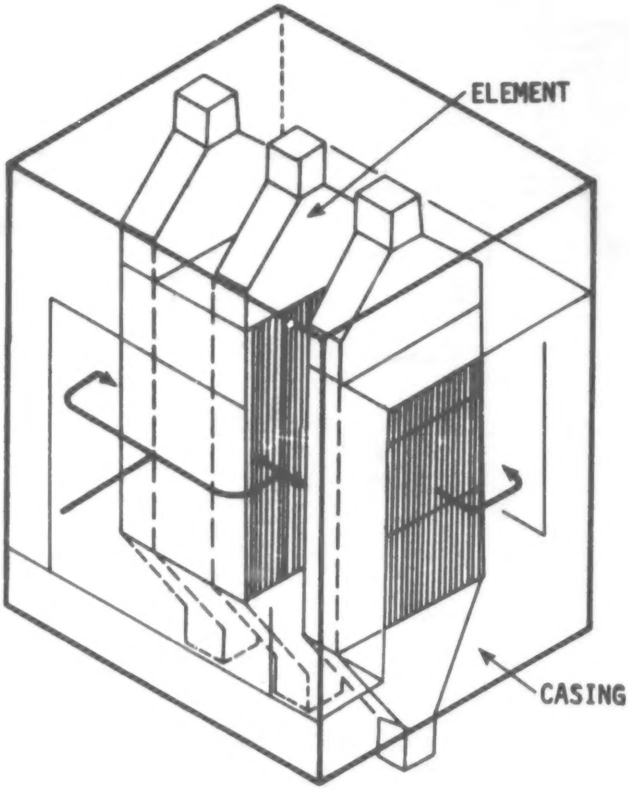

ELEMENT
CASING

Figure 46. Structure of Kurabo moving-bed reactor.

the reactor at 350° to 400°C with an NH_3/NO_x mole ratio of about 1.0. Following are typical operating data:

NO_x concentration, ppm	280 (inlet)	18 (outlet)
Dust content, mg/Nm^3	94 (inlet)	17 (outlet)
Gas volume, Nm^3/hr	24,000	
Space velocity, hr^{-1}	8000	
SO_2 concentration, ppm	1650	
Gas temperature, °C	400	
Pressure drop in reactor, mm H_2O	65	
Ammonia consumption, liters/min	106.4	

The catalyst discharged from the reactor is screened to remove dust, heated to 800°C to recover the catalyst, and then returned to the reactor. One cycle takes about 100 hours, an indication that only a small portion of the catalyst always undergoes regeneration. The catalyst has a high strength of more than 10 kilograms per granule, and the annual crushing loss is less than 5 percent. The catalyst life is estimated at about 10,000 hours. The gas from the reactor is passed through a tubular heat exchanger. The outlet gas temperature is maintained at 200°C to prevent the deposit of ammonium bisulfate.

For a utility boiler that undergoes considerable load fluctuation, an auxiliary burner may be needed to control the gas temperature in the reactor. Because of high SO_2 and NH_3 concentrations in the reactor, the temperature must be kept above 350°C to prevent amminium bisulfate deposits.

Estimated denitrification costs are shown in Tables 12 and 13. The estimate is based on the assumption that the gas from the uncontrolled boiler would be cooled from 360°C to 200°C in an air heater and that with denitrification the gas would be heated by an auxiliary burner to 400°C and emitted at 220°C from the air heater.

Table 12. DENITRIFICATION PLANT COST
(thousands of dollars)

Item	Capacity, Nm^3/hr		
	30,000	100,000	500,000
Reactor, heater, etc.	330	887	3347
Duct	83	197	543
Instrumentation	93	203	540
Transportation and installation	44	113	310
Subtotal	550	1400	4740
Catalyst	40	130	640
Total	590	1530	5380

The estimate shows that the denitrification cost is about $11 per kiloliter (2.3 mills/kWh) for a 100,000 Nm^3/hr unit and $8.53 per kiloliter (1.8 mills/kWh) for a 500,000 Nm^3/hr unit, assuming 8400 hours operation in a year.

Table 13. DENITRIFICATION COST (KURABO PROCESS)

C grade heavy oil: 0.78 kl/10,000 Nm^3, NO_x 280 ppm, 8400 hours annual operation; Average yearly load: 80%; Gas temperature: 360°C before air heater, 400°C in reactor, 220°C after air heater

	Capacity, 1000 Nm^3/hr					
	30		100		500	
	$1000/year	$/kl	$1000/year	$/kl	$1000/year	$/kl
Depreciation	75.9	4.82	196.7	3.75	692.1	2.64
Interest	29.5	1.88	76.5	1.46	269.2	1.03
Ammonia	21.2	1.35	61.8	1.18	154.4	0.59
Power (3¢/kW-hr)	24.4	1.55	71.3	1.36	294.6	1.12
Catalyst ($8300/$m^3$)	25.0	1.59	83.3	1.59	416.7	1.59
Steam (0.3¢/kg)	0.7	0.05	2.4	0.05	14.6	0.06
Labor	6.0	0.38	6.0	0.11	9.0	0.03
Maintenance, etc.	3.3	0.21	8.3	0.16	23.3	0.09
Fuel*	21.7	1.38	72.5	1.38	326.5	1.38
Total	207.8	13.21	578.9	11.04	2236.4	8.53

* For auxiliary burner. Half of this energy is recovered.

Emission of the gas at 220°C causes a fairly large loss of energy. Use of the Ljungstrom-type heat exchanger will allow more energy recovery, although soot blowing is required. Kurabo has been developing a microcomputer system to minimize emissions of ammonia from the reactor without decreasing the denitrification efficiency as boiler load fluctuates. It would then be possible to attain better heat recovery with a heat exchanger and thus prevent the deposit of the bisulfate. In treating flue gas from a coal-fired boiler, a multicyclone may be used to reduce the dust content of the gas to a degree compatible with the moving-bed reactor.

SCR PROCESSES WITH SANTETSU (SARC) CATALYST

Santetsu Iron Catalyst (SARC)

Santetsu Kogyo, a chemical company, has developed an effective catalyst made of solid goethite ($Fe_2O_3 \cdot H_2O$). The ferric oxide is recovered from waste liquor containing ferric iron by neutralization with ammonia. The price of the catalyst, now about $8000 per ton, may be substantially reduced when the catalyst is produced in large quantities.

The catalyst is effective above 300°C and is resistant to SO_x. It is easily shaped into rings with a diameter of 13 to 35 millimeters and with a smooth surface to minimize the effect of dust. The catalyst is used by the companies discussed in the following paragraphs.

Mitsubishi Kakoki Kaisha (MKK) has operated two pilot plants to treat boiler flue gas and is constructing (1) a pilot plant (1000 Nm^3/hr) to treat waste gas from iron-ore sintering, using funds of the Japan Iron and Steel Federation, and (2) a commercial plant (15,000 Nm^3/hr) to treat flue gas from an oil-fired boiler (Table 8).

Seitetsu Kagaku Kogyo, a chemical company, has operated successfully since July 1975 a pilot plant with capacity of treating 15,000 Nm^3 per hour of flue gas from an oil-fired boiler.

Other companies including Ishikawajima-Harima Heavy Industries (IHI) also plan to build pilot plants using the SARC catalyst.

Tests by MKK with SARC Catalyst

MKK has operated a pilot plant with capacity of treating 1400 Nm^3 per hour of flue gas from low-sulfur oil burning. They have used the following three sizes of ring-type SARC catalyst produced by Santetsu Kogyo:

No.	Diameter, mm		Height or thickness, mm
	Inner	Outer	
II	20	35	15
III	13	23	13
IV	8	13	13

The flue gas at 330° to 450°C contains 170 to 400 ppm NO_x, 30 to 50 ppm SO_x, 7 to 8 percent CO_2, 6 to 7 percent O_2, 8 to 10 percent H_2O, and about 40 mg/Nm^3 dust. The gas is introduced into the reactor without dust removal. The reactor has a diameter of 635 millimeters, and the packed height ranges from 600 to 1200 millimeters. In test operation, catalyst II was packed regularly, and III and IV were packed at random. Gas volume was variable, from 800 to 1400 Nm^3/hr. Test results are shown in Figures 47, 48, and 49.

With catalyst IV more than 90 percent of NO_x was removed at a space velocity of 5700 hr^{-1} at 420°C and an NH_3/NO_x ratio of 1.2. The randomly packed III and the regularly packed II gave nearly equal removal ratios -- about 90 percent at a space velocity of 3500 hr^{-1} at 420°C and an NH_3/NO_x mole ratio of 1.2. Although catalyst III is smaller than catalyst II, the packed density and pressure drop were lower with III because of the random packing.

The pressure drops with a 1-meter packed height at a gas velocity of 2 meters per second were 80 millimeters H_2O for III, 135 millimeters H_2O for II, and 150 millimeters H_2O for IV (Figure 50). The dust content of the gas is about 1000 milligrams per cubic meter normally and much higher when soot is blown from the boiler three times a day. But no effect of dust was observed in continuous tests for 1000

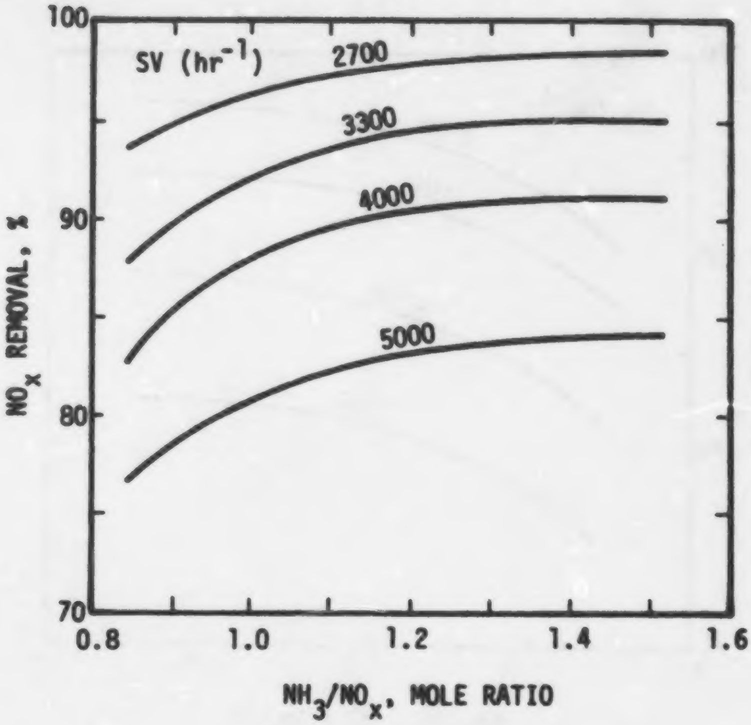


Figure 47. Results with SARC II catalyst (420°C).

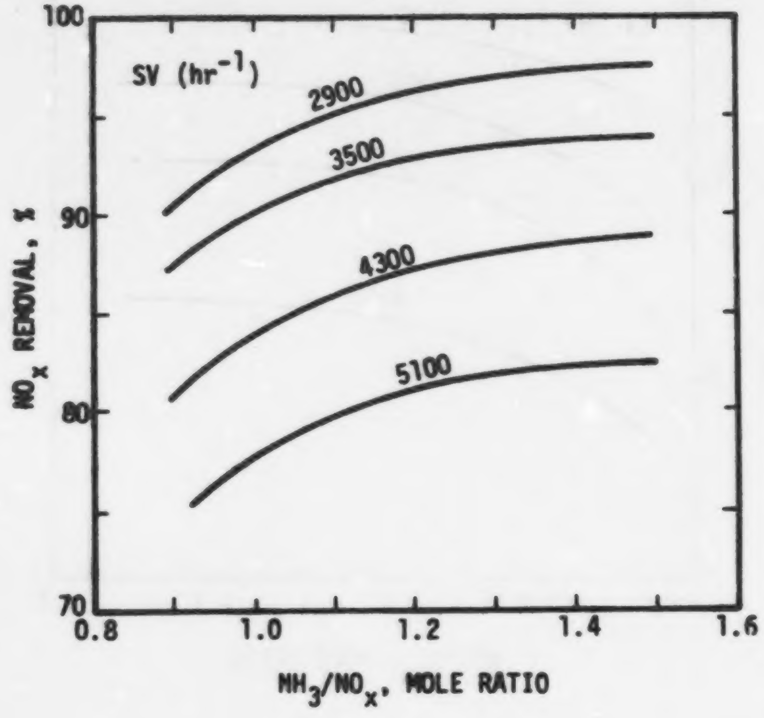


Figure 48. Results with SARC III catalyst (420°C).

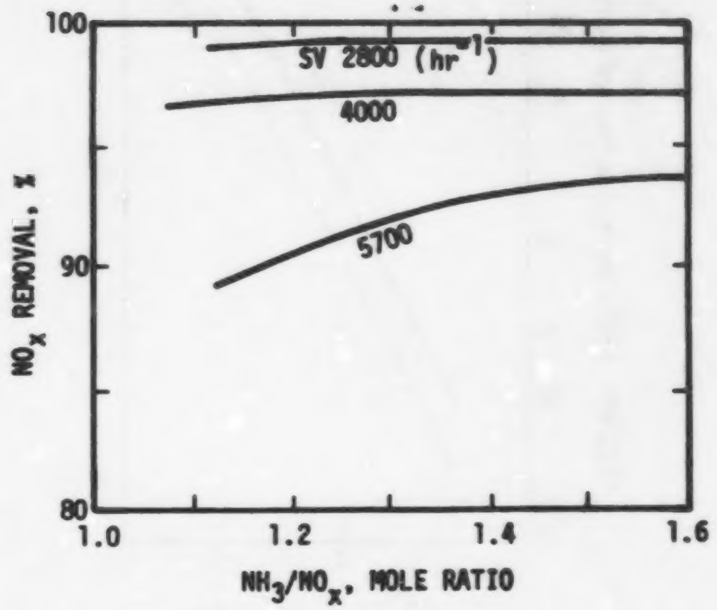


Figure 49. Results with SARC IV catalyst (420°C).

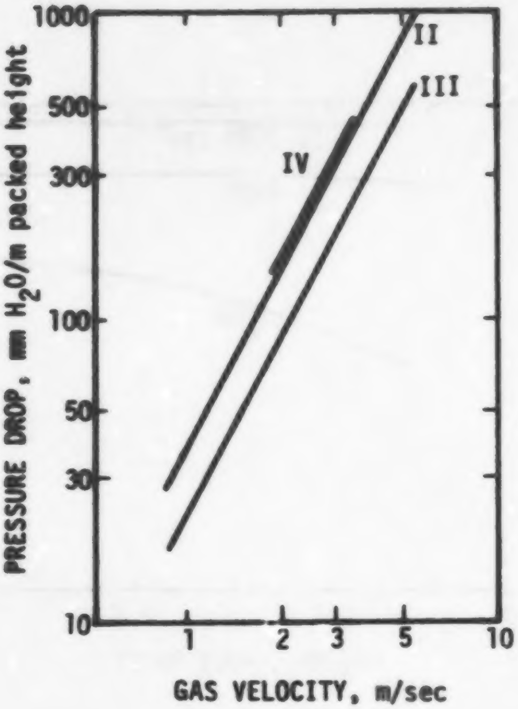


Figure 50. Gas velocity and pressure drop with SARC catalysts.

hours with catalyst II, 1700 hours with III, and 1000 hours with IV. In the event of dust plugging, the catalysts can be washed with water to remove dust. This has not yet been necessary.

The slip ammonia (NH_3 concentration of the reactor effluent gas) when reacted at 420°C was less than 0.2 ppm at an NH_3/NO_x ratio of 1.2 and about 1 ppm at a ratio of 1.4 to 1.6; the SARC catalyst is capable of decomposing the excessive ammonia.

The relationship of reaction temperature and space velocity to denitrification ratio is shown in Figure 51. More than 80 percent removal was obtained at a temperature of 330°C and a space velocity of 4000 hr^{-1}.

OTHER SCR PROCESSES

Sumitomo Chemical has made extensive tests on SCR and has constructed several commercial plants, including the world's first plant for combustion gas treatment, completed in 1974 (Table 8). Details of the process and the chemistry involved were described earlier (1). Recently commercial plants for dirty-gas treatment have started operation, but no details of operation have been disclosed.

Mitsui Toatsu Chemical also developed its own catalysts and constructed a few units (Table 8). They plan to cooperate with IHI in building larger plants.

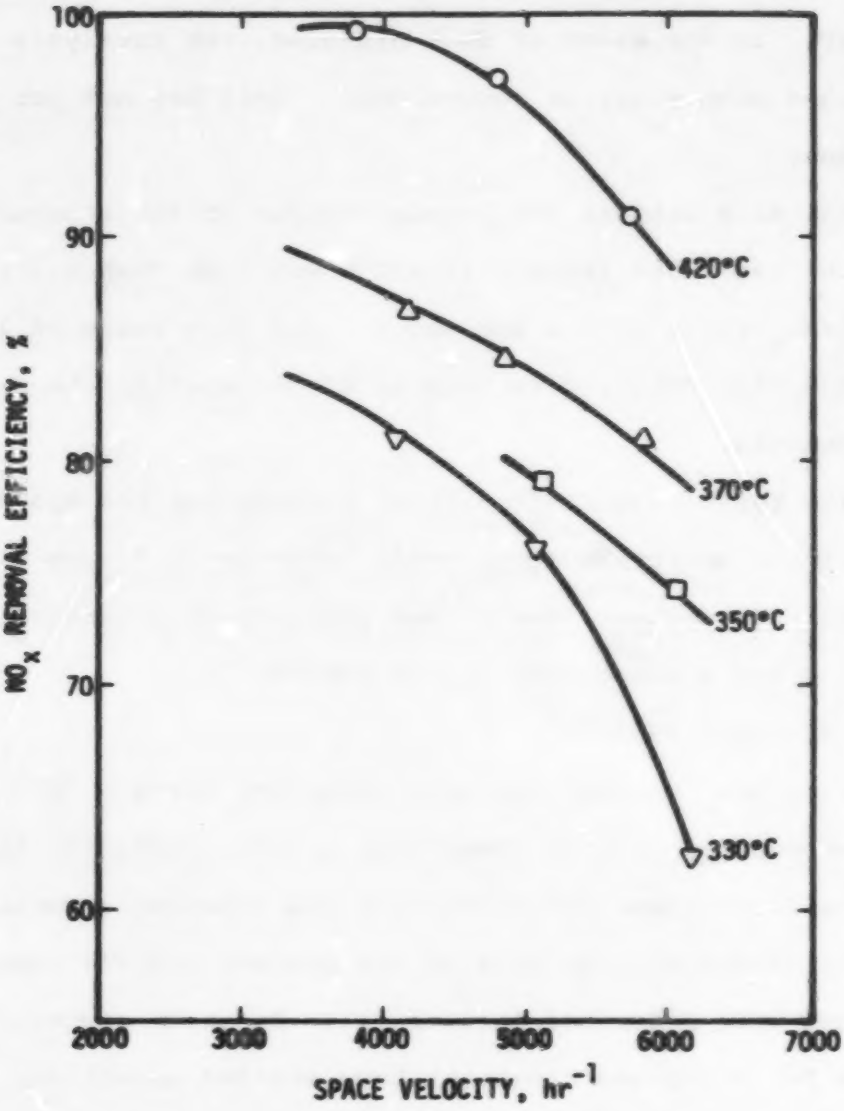


Figure 51. Results with SARC IV catalyst

(NH_3/NO_x mole ratio, 1.2)

Mitsui Shipbuilding is constructing a few units (Table 8) using a catalyst developed by Mitsui Petrochemical. Plant cost is estimated at about $5 million for a 67-megawatt boiler, with guarantees of 90 percent NO_x removal and 1 year catalyst life for treatment of gas containing less than 100 ppm SO_x.

Asahi Glass Company has also developed its own catalyst and is constructing a unit to treat flue gas from a glass-melting furnace (Table 8).

AMMONIA INJECTION WITHOUT CATALYST

Nippon Kokan applied for a patent in 1970 for a denitrification process in which ammonia is injected into waste gases at temperatures above 500°C and some refractory structure is used instead of a catalyst to promote the mixing of ammonia and the gas. A few years later Exxon also made patent application for ammonia injection without a catalyst. Both patents are pending.

Laboratory tests have shown that when ammonia is injected at 980° to 1000°C about 80 percent of the NO is converted to N_2 and that the residual ammonia in the treated gas is below 20 ppm. In a large-scale operation about 50 percent of the NO_x removal is expected at an NH_3/NO mole ratio of 1.5 to 2.0 because the suitable temperature range is narrow and very rapid mixing of NH_3 and gas is required.

Fluctuation of exhaust gas temperature with load in a utility boiler may present a problem. When the temperature drops, unreacted ammonia may be emitted. When it rises excessively, a portion of the ammonia may be converted to NO.

Exxon has found that addition of hydrogen with ammonia can reduce the reaction temperature to 730°C (15). The use of hydrogen at power plants may be difficult, however.

The ammonia injection process would be suited for industrial boilers that are not subject to large load fluctuations. It also is suitable for treating flue gases, such as those from coal-fired boilers and cement kilns, which contain dust that contaminates the SCR catalyst. There is a possibility that ammonium bisulfate is deposited in the air heater, as in the SCR processes.

Electric Power Development Company (EPDC), which owns several coal-fired boilers, is testing the Exxon process for possible commercial use in 1978 (Table 9). Many other companies also have been testing ammonia injection processes, because injection without a catalyst may be the most economical method of flue gas denitrification, even though removal efficiency may not be high.

REACTION OF ACTIVATED CARBON WITH NO_x (16)

Classification of Reactions

Activated carbon has the following functions useful in removing NO_x:

(1) Adsorption	It adsorbs NO_2 below 100°C.
(2) Oxidation	It promotes the oxidation of NO to NO_2 below 100°C.
(3) Catalytic reduction	Above 100°C, it promotes the following reactions:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

$$2NO + C \rightarrow N_2 + CO_2$$

NO_x Adsorption

Below 100°C activated carbon adsorbs NO_2 fairly well, but does not adsorb NO very well. In the presence of O_2, however, NO is oxidized to NO_2 by the catalytic reaction of carbon, and the resulting NO_2 is adsorbed. The adsorption efficiency of carbon is shown in Figure 52 in comparison with that of silica gel. The amounts of NO_x adsorbed by carbon under different conditions are shown in Table 14. A larger amount is adsorbed at lower temperatures and humidities.

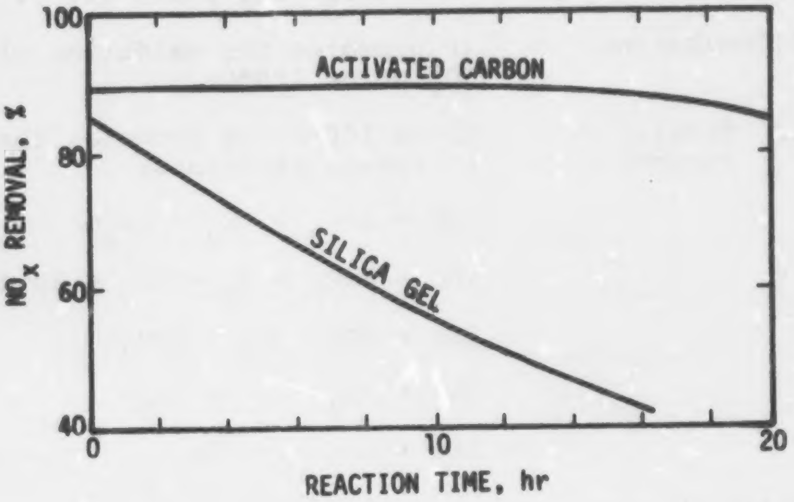


Figure 52. NO_x adsorption capacity

(Temp., 18°C; NO, 1800 ppm; NO_2, 1200 ppm; SV, 1000 hr^{-1})

Table 14. NO_x ADSORPTION CAPACITY OF ACTIVATED CARBON

(mg NO_x/g activated carbon)

Relative humidity, %	Adsorption temperature		
	30°C	50°C	70°C
14	120.0		56.8
20		110.2	
35	104.0	95.0	
40			36.8
60		75.4	
75	67.7		

NO_x Desorption

NO_x adsorbed by carbon is desorbed either by washing with water or by heating. Water washing produces a dilute nitric acid. Higher temperatures are more favorable for the washing, as shown in Figure 53. The wet carbon after washing has poor NO_x adsorption ability and should be dried before it is used again for adsorption. For SO_2 adsorption, however, the wet carbon is effective.

Figure 54 shows the desorption rates when carbon is heated in a nitrogen gas stream at different temperatures. Above 150°C desorption occurs fairly rapidly, but carbon is consumed in reaction (8) to form NO. When the gas is heated above 450°C, a larger amount of carbon is consumed in reaction (9) to form N_2.

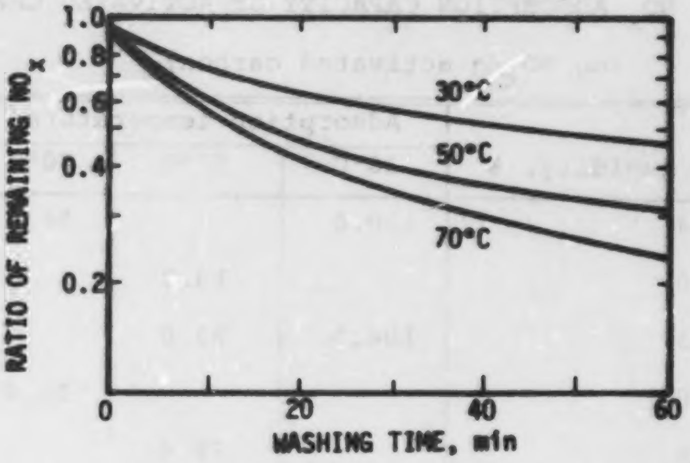


Figure 53. Desorption of NO$_x$ adsorbed by activated carbon by washing with water at different temperatures (activated carbon 6 mm in diameter).

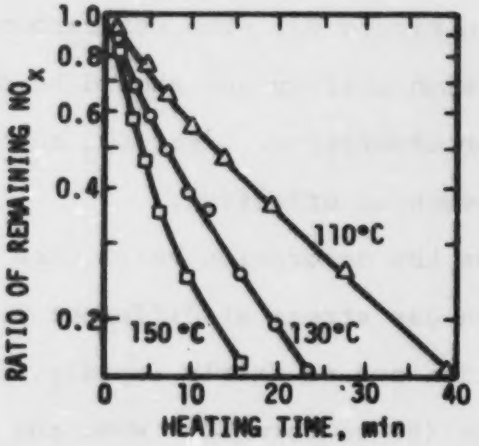


Figure 54. Desorption of NO$_x$ adsorbed by activated carbon by heating at different temperatures.

$2NO_2 + C \rightarrow 2NO + CO_2$ (8)

$2NO_2 + 2C \rightarrow N_2 + 2CO_2$ (9)

Heating carbon in a stream of reducing gas lowers the carbon consumption substantially and increases the conversion of NO_x to N_2 (Table 15).

Catalysts for Ammonia Reduction

Among the reducing gases mentioned previously, ammonia is most useful in flue gas treatment because other reducing gases are readily consumed by O_2 in the flue gas. The effect of carbon on the reaction between NO_x and NH_3 is further increased by adding base metal compounds (Table 16). Copper and vanadium have been found most effective.

SIMULTANEOUS REMOVAL PROCESSES USING ACTIVATED CARBON

Simultaneous Removal of SO_x and NO_x

Activated carbon has been used commercially as an adsorbent for SO_2. Although it also adsorbs NO_x, the adsorbing capacity is not sufficient to treat a large amount of gas. Takeda Chemical has produced activated carbon adsorbents that contain metallic components or that are specially structured to promote the reaction of NO_x with ammonia to form N_2. Higher temperature is favorable to the reaction but decreases the SO_2 adsorbing capacity (Figure 55). Optimum temperature for simultaneous removal by this process is about 250°C.

Table 15. DESORPTION OF NO_x IN REDUCING GAS

Gas	Temperature, °C	Conversion ratio of adsorbed NO_x into N_2 on desorption, %
H_2	200	10
	400	68
	600	100
CO	200	12
	400	70
	600	100
NH_3	200	100
	400	100
	600	100
He	200	0
(Inert gas)	400	5
	600	70

Table 16. EFFECT OF ADDITION OF BASE METAL COMPOUNDS TO CARBON ON NO_x REDUCTION EFFICIENCY (NO 2000 ppm, NH_3 3000 ppm, SV 3000 hr^{-1})

Metal	NO_x reduction efficiency, %		
	110°C	150°C	250°C
None	38	44	78
Ti		65	
Cr	55	70	95
Mn	50	67	88
Fe	52	67	90
Co	63	75	98
Ni		67	
Cu	91	99	100
V	80	88	100
Mo		70	
W		65	

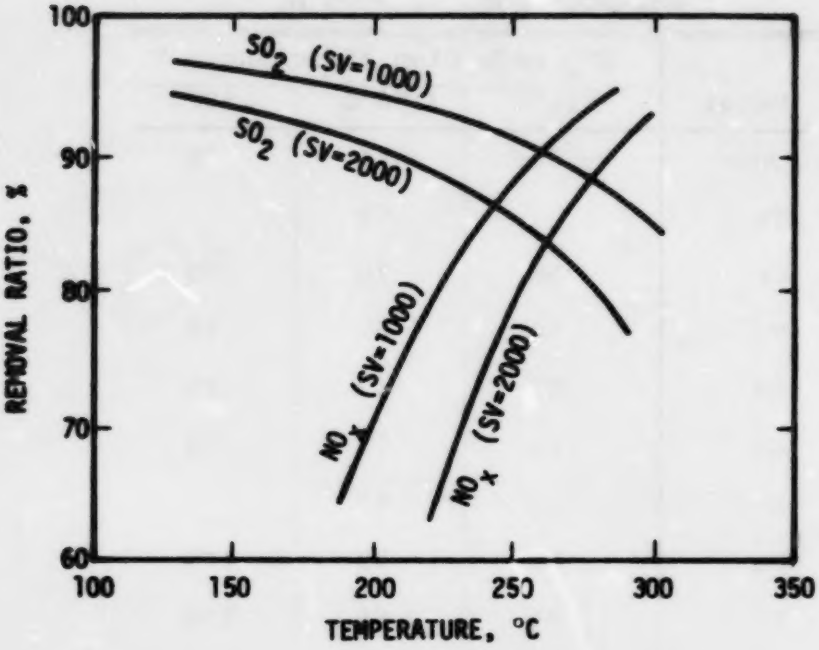


Figure 55. SO_2 and NO_x removal by activated carbon at different temperatures and space velocities.

Carbon for simultaneous removal of SO_2 and NO_x costs about $8000 per ton, whereas carbon used commercially for flue gas desulfurization costs $3000 per ton. Simultaneous removal from flue gas leaving a 300-MW boiler will require about 1000 tons of the carbon, which may be too expensive. The price would be substantially lower in mass production.

Unitika Activated Carbon Process

Unitika Company recently started operating a pilot plant with a capacity to treat 4500 Nm^3/hr of flue gas from a glass-melting furnace, containing about 400 ppm SO_2 and 500 ppm NO_x (Figure 56). The plant has a tower with four compartments, all of which have a fixed carbon bed. About 600 ppm NH_3 is added to the gas at about 230°C, and the mixed gas is ducted to three compartments. About 98 percent of the NO_x and SO_2 is removed. The carbon that has adsorbed SO_2 is heated to 350°C in a reducing hot gas to release concentrated SO_2 for sulfuric acid production. Ammonium sulfate and sulfite, which tend to form on the carbon, are decomposed to SO_2 and N_2 in the regeneration step.

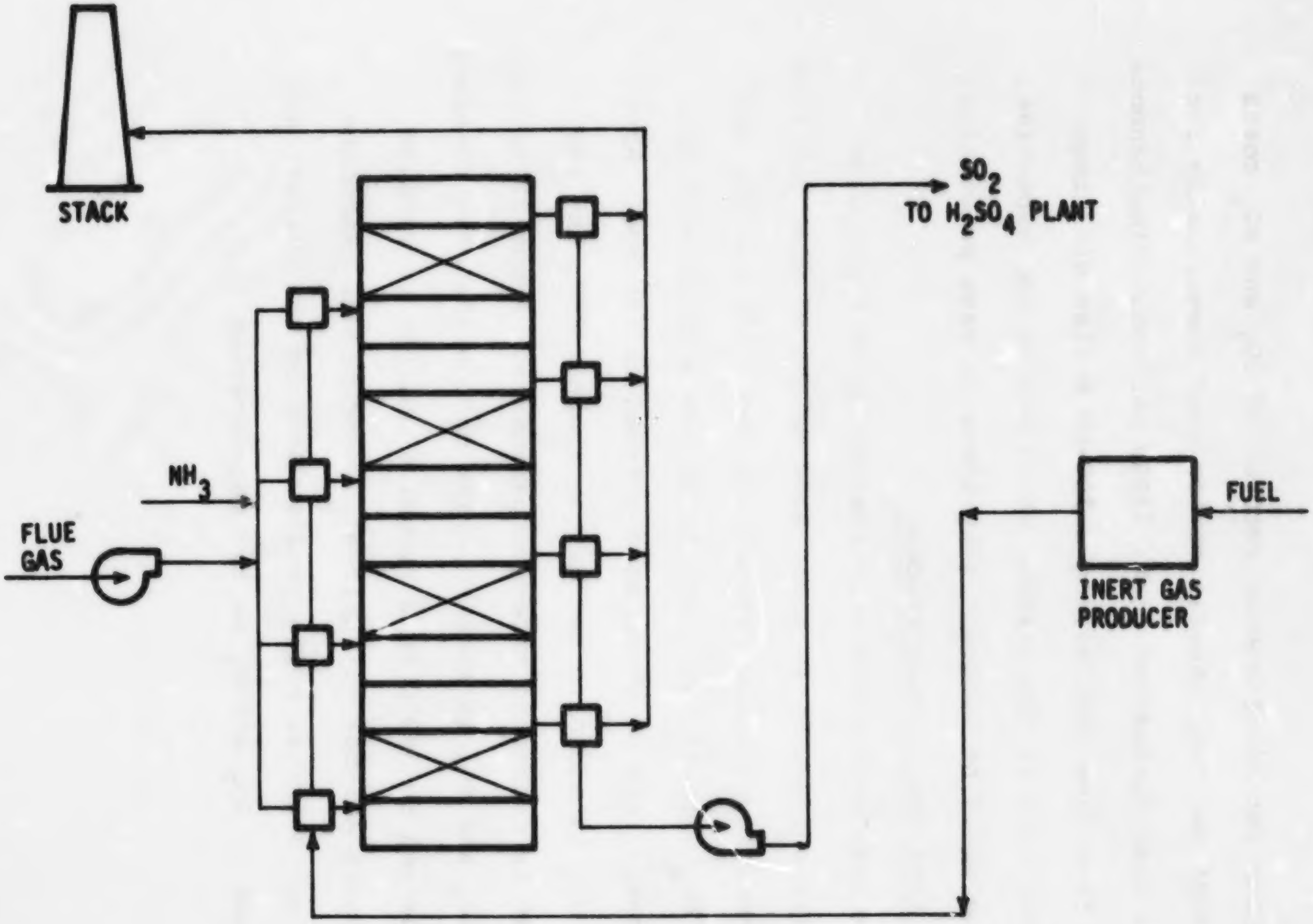

STACK
SO_2 TO H_2SO_4 PLANT
NH_3
FLUE GAS
FUEL
INERT GAS PRODUCER

Figure 56. Flowsheet of Unitika process.

The principal design and operating parameters are as follows:

Tower height	17 m
Carbon bed thickness	1 m
Pressure drop	100 mm H_2O
Adsorption time for one cycle	3 days
Regeneration time for one cycle	12 hours
SO_2 in gas from regeneration step	5 to 10 percent

A space velocity of about 700 hr^{-1} is used. The carbon consumption is estimated to be less than 10 percent of a charge per year. In the 6 months of operation, carbon loss has been only 1 to 2 percent. Gas from the regeneration step, containing 5 to 10 percent SO_2, may be used for sulfuric acid production.

Other Activated Carbon Processes

Sumitomo Heavy Industries has constructed a prototype flue gas desulfurization plant (175,000 Nm^3/hr) using moving beds of adsorbent activated carbon, which is regenerated by heating in a reducing gas. With this plant, the company has studied simultaneous removal and is constructing a test plant with a capacity to treat 1500 Nm^3/hr of flue gas using moving beds.

Hitachi, Limited, has found that activated carbon treated with ammonium bromide is effective even at 100°C for NO_x reduction by ammonia (17). The low-temperature activity may result in energy saving, but deposits of ammonium sulfate and bisulfate on the carbon may present a problem.

EBARA-JAERI ELECTRON BEAM PROCESS (18)

Ebara Manufacturing Company and the Japan Atomic Energy Research Institute, a government organization, have developed jointly a unique process for the simultaneous removal of SO_2 and NO_x by electron beam radiation. A pilot plant with capacity to treat 1000 Nm^3/hr of flue gas from an oil-fired boiler has been operated by Ebara. A larger pilot plant with capacity to treat 3000 Nm^3/hr of waste gas from an iron ore sintering plant is scheduled for construction at Yawata Works, Nippon Steel Corporation.

A flowsheet of a bench-scale test unit is shown in Figure 57. Dimensions of the stainless steel reactor are 50 by 500 millimeters. The electron beam accelerator (Cockcroft-Walton type) is made by Hitachi, Limited. Flue gas produced by burning of oil and containing 600 to 900 ppm SO_2 and 80 ppm NO_x was passed through an ESP, introduced into the reactor, and exposed to the electron beam. A sulfuric acid mist and a powdery product containing sulfur, nitrogen, oxygen and hydrogen were produced and treated by another ESP.

Figure 58 shows the results of tests at 110°C. About 90 percent of the NO_x was removed by an electron beam of

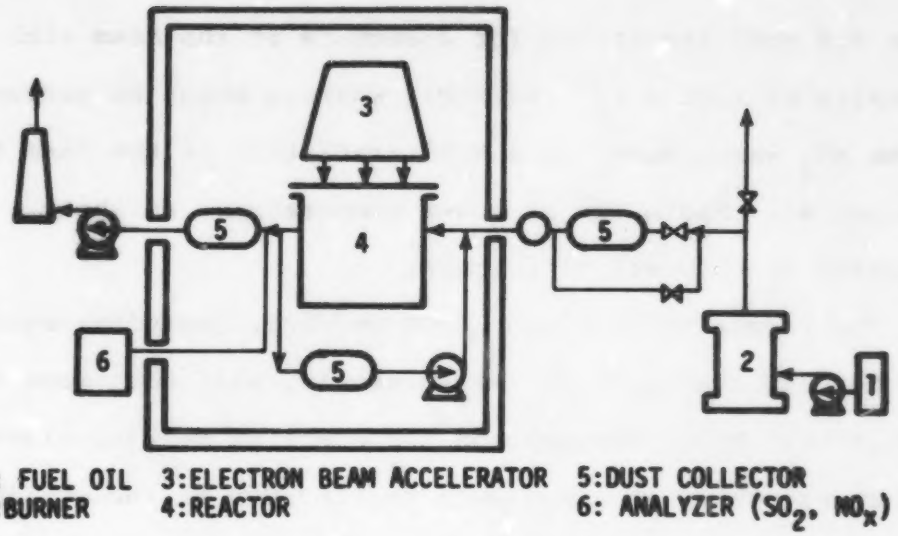

3
4
5
5
5
6
2
1
1: FUEL OIL
2:BURNER
3:ELECTRON BEAM ACCELERATOR
4:REACTOR
5:DUST COLLECTOR
6: ANALYZER (SO_2, NO_x)

Figure 57. Apparatus for tests of electron beam process.

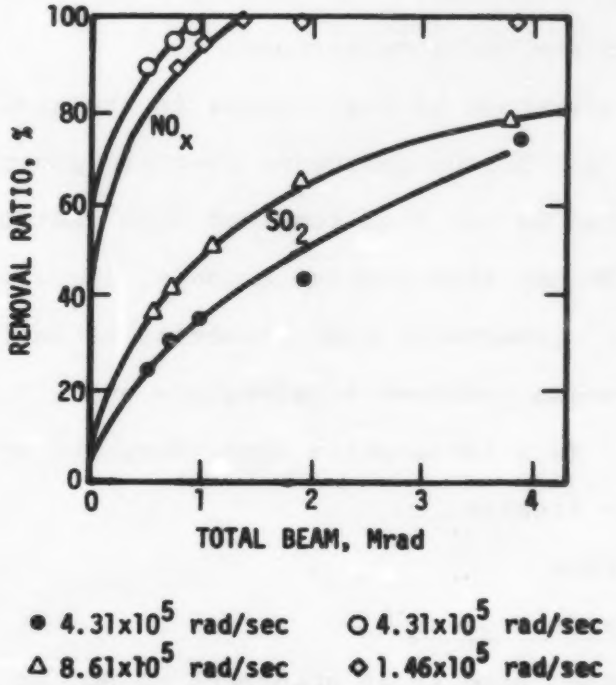


Figure 58. Results with different intensities of electron beam.

about 0.8 Mrad (radiation for 2 seconds of the beam with an intensity of 4.31 x 10^5 rad/sec), whereas about 80 percent of the SO_2 was removed at 4 Mrad (radiation of the beam for 10 seconds). Radiation at lower temperatures slightly increased the removal efficiency.

The larger pilot plant (3000 Nm^3/hr), including equipment for various tests and measurements, will cost more than $1 million. Power consumption for electron beam acceleration is estimated at 1 megawatt for 100,000 Nm^3/hr of flue gas (about 32 MW equivalent). It may be possible to make an electron beam accelerator as large as 1 MW. Consequently, treatment of 1,000,000 Nm^3/hr of flue gas from a 320-MW boiler will require ten accelerators.

The main advantage of the process is the simultaneous removal of NO_x and SO_2 by consuming electric power only. Power consumption is not high compared with that of other processes, which may also require ammonia, lime, or some other chemical. Investment cost, however, seems fairly high because the process requires accelerators and a highly efficient ESP. In a large-scale operation, the by-product will have to be treated.

OTHER DRY PROCESSES

Shell Copper Oxide Process

Copper oxide, used as an absorbent of SO_2 in the Shell process, works as a catalyst in the reaction of NO_x with ammonia. The Yokkaichi plant of SYS, treating 120,000 Nm^3/hr of flue gas from an oil-fired boiler by the Shell process, has introduced ammonia into a reactor at 400°C since 1975. Up to about 70 percent of the NO_x can be removed. Copper sulfate formed by SO_2 absorption is reacted with hydrogen to generate concentrated SO_2, which is sent to a Claus furnace to produce sulfur.

The plant uses two parallel-passage reactors alternately for absorption and desorption-regeneration. The reactor is fairly free of dust plugging. The flue gas at 400°C is treated without using a hot ESP ahead of the reactor.

Dry Adsorption Process

Small-scale tests have been conducted in which NO_x was adsorbed by materials other than activated carbon, including molecular sieve, silica gel, and calcium silicate. Nissan Chemical Industries, a large chemical company, is going to use molecular sieves (to be supplied by Union Carbide, U.S.A.), for the treatment of tail gas from a nitric acid plant (20,000 Nm^3/hr). The unit is operated at a pressure of 5 atmospheres and is suitable for adsorption. The adsorbed NO_x will be released by heating and will be returned to the acid plant.

Generally speaking, adsorption processes are not suitable for large amounts of gas, particularly those containing SO_2 and dust.

Catalytic Decomposition

The decomposition of NO_x into N_2 and O_2 is an exothermic reaction that can theoretically proceed even at room temperature, but the reaction rate is quite small. Tests have been made on catalysts that may promote the reaction at relatively low temperature (150° to 200°C). No data have been published. Some of the catalysts work fairly well at 700° to 800°C, but it seems that no effective low-temperature catalyst has been found.

SECTION 4

WET PROCESSES FOR NO_x REMOVAL

GENERAL DESCRIPTION

Major Processes and Plants

Major plants using wet processes for NO_x removal from flue gas are listed in Table 17. In addition there are many small commercial units for treating waste gas from plants using nitric acid. The major processes may be classified as follows:

Oxidation-absorption

Absorption-oxidation

Oxidation-reduction (simultaneous removal of NO_x and SO_x)

Reduction (simultaneous removal of NO_x and SO_x)

Essentially all of the NO_x in the combustion gas is in the form of NO, which has poor reactivity and is not readily absorbed by most absorbents. NO is oxidized to NO_2 in air, but the oxidation occurs slowly. In many processes oxidizing agents are used to promote absorption of NO_x.

Oxidizing Agents

Ozone (O_3) and chlorine dioxide (ClO_2) are used mainly for the oxidation of NO in the gaseous phase. They oxidize NO to NO_2 within a second but barely oxidize SO_2 to SO_3.

Table 17. MAJOR PLANTS FOR NO_x REMOVAL FROM FLUE GAS BY WET PROCESSES

Process developer	Type of process	Plant owner	Plant site	Capacity, Nm^3/hr	Source of gas	Completion	By-product
(Tokyo Electric Mitsubishi H.I.)	(Oxidation absorption)	Tokyo Electric	Minami-Yokohama	2,000	Boiler[b]	Dec. 1973	HNO_3
(Tokyo Electric Mitsubishi H.I.)	(Oxidation absorption)	Tokyo Electric	Minami-Yokohama	100,000	Boiler[b]	Oct. 1974	HNO_3
Kawasaki H.I.	(Oxidation absorption)	EPDC	Takehara	5,000	Boiler[c]	Dec. 1975	[Gypsum $Ca(NO_3)_2$]
Nissan Engineering	(Absorption oxidation)	Ijima Metal	Tokyo	1,000	Pickling	July 1973	$NaNO_2$
Nissan Engineering	(Absorption oxidation)	Nissan Chemical	Toyama	3,000	HNO_3 plant	Mar. 1975	$NaNO_3$, NO
(Mitsubishi Metal MKK, Nihon Chem.)	(Absorption oxidation)	Mitsubishi Metal	Omiya	4,000	Boiler[a]	Dec. 1974	HNO_3
Kobe Steel	(Absorption oxidation)	Kobe Steel	Kakogawa	1,000	Furnace[e]	Dec. 1973	Gypsum, N_2
Kobe Steel	(Absorption oxidation)	Kobe Steel	Kakogawa	50,000	Furnace[e]	Mar. 1976	Gypsum, N_2
Hodogaya	(Absorption oxidation	Hodogaya	Koriyama	4,000	Furnace[e]	Oct. 1975	$NaNO_3$, NaCl
(Sumitomo Metal Fujikasui)	(Oxidation reduction)	Sumitomo Metal	Amagasaki	62,000	Boiler[a]	Dec. 1973	($NaNO_3$, NaCl, Na_2SO_4)
(Sumitomo Metal Fujikasui)	(Oxidation reduction)	Toshin Steel	Fuji	100,000	Furnace[d]	Dec. 1974	($NaNO_3$, NaCl, Na_2SO_4)
(Sumitomo Metal Fujikasui)	(Oxidation reduction)	Sumitomo Metal	Osaka	39,000	Boiler[a]	Dec. 1974	($NaNO_3$, NaCl, Na_2SO_4)
Osaka Soda	(Oxidation reduction)	Osaka Soda	Amagasaki	60,000	Boiler[a]	Mar. 1976	($NaNO_3$, NaCl, Na_2SO_4)
Shirogane	(Oxidation reduction)	Mitsui Sugar	Kawasaki	40,000	Boiler[a]	Aug. 1974	Na_2SO_4, $NaNO_3$
Chiyoda	(Oxidation reduction)	Chiyoda	Kawasaki	1,000	Boiler[a]	1973	[Gypsum, $Ca(NO_3)_2$]
Mitsubishi H.I.	(Oxidation reduction)	Mitsubishi H.I.	Hiroshima	2,000	Boiler[a]	Dec. 1974	Gypsum, NH_3
Ishikawajima H.I.	(Oxidation reduction)	Ishikawajima H.I.	Yokohama	5,000	Boiler[a]	Sept. 1975	Gypsum, N_2
Kureha Chemical	Reduction	Kureha Chem.	Nishiki	5,000	Boiler[a]	Apr. 1975	Gypsum, N_2
Chisso Corp.	Reduction	Chisso P.C.	Goi	300	Boiler[a]	1974	$(NH_4)_2SO_4$
Mitsui S.B.	Reduction	Mitsui P.C.	Chiba	150	Boiler[a]	1974	H_2SO_4, N_2
Asahi Chemical	Reduction	Asahi Chemical	Mizushima	600	Boiler[a]	1974	Gypsum, N_2

[a] Oil-fired boiler.
[b] Gas-fired boiler.
[c] Coal-fired boiler.
[d] Metal-heating furnace.
[e] Iron-ore sintering furnace.

Ozone can oxidize NO to N_2O_5 when added in an excessive amount.

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$2NO + 3O_3 \rightarrow N_2O_5 + 3O_2$$

Ozone is fairly expensive, and costs $1.20 to 1.40 per kilogram (about 1.5 mills/kWh). A large-scale ozone generator with a capacity of 100 kilograms per hour of ozone is near completion. It can treat about 230,000 Nm^3/hr of flue gas (76 MW equivalent) containing 200 ppm NO. The cost of ozone is expected to decrease to some extent with the large generator. The cost of chlorine dioxide is 30 to 40 percent less than that of ozone, but chlorine dioxide has the disadvantage of introducing hydrochloric and nitric acids, which complicate the system.

$$2NO + ClO_2 + \underset{\text{moisture}}{\overline{H_2O}} \rightarrow NO_2 + HNO_3 + HCl$$

Solutions of potassium and sodium permanganates, sodium and calcium hypochlorites, and hydrogen peroxide have been used for the oxidation in the liquid phase, but these chemicals are also expensive.

Oxidation-Absorption and Absorption-Oxidation Processes

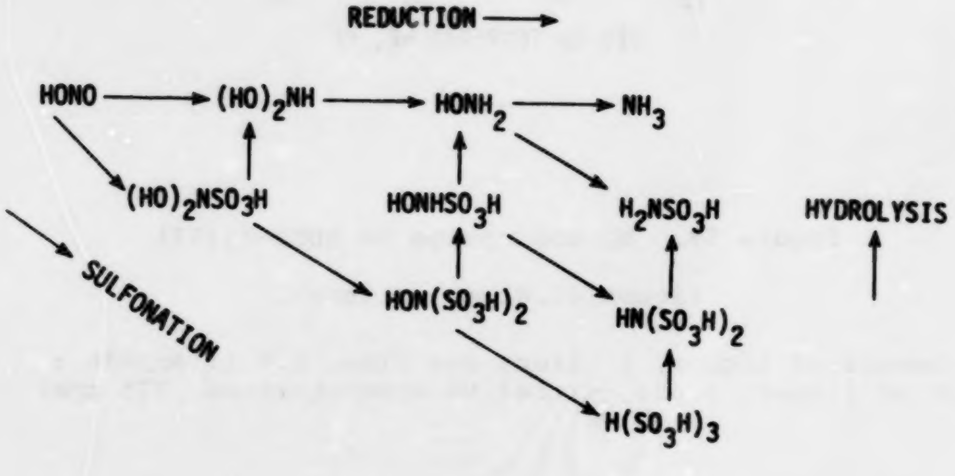
In oxidation-absorption processes the NO is first oxidized with a gaseous oxidizing agent and then absorbed. In absorption-oxidation processes the NO is absorbed in a solution containing an oxidizing agent. Usually NO_x absorption occurs more slowly in the latter case because NO must be absorbed in the liquor before it can be oxidized. Most plants using nitric acid for such processes as metal washing emit a gas fairly rich in NO_x (1000 to 10,000 ppm). However, the amount of gas is not great (500 to 5000 Nm^3/hr). In many of the plants, all or part of the NO is oxidized to NO_2, and the gas is absorbed in a sodium hydroxide solution. Activated carbon is used in some plants as a catalyst for the oxidation of NO by air. In other plants NO_x is absorbed in a solution containing an oxidizing agent such as NaClO or H_2O_2. In both cases the resulting liquor, containing nitrate and nitrite, is sent to a wastewater treatment system. Such processes cannot be applied on a large scale because the treatment does not remove the nitrogen compounds from the wastewater.

Tests have been made in pilot plants to recover nitric acid for industrial use or to recover potassium or calcium nitrate for fertilizer. Those processes do not seem promising because of the high cost and the limited demand for the by-products.

Oxidation-Reduction and Reduction Processes (Simultaneous Removal)

Since 1973 many oxidation-reduction and reduction processes have been developed in which NO_x and SO_x are absorbed simultaneously. In the oxidation-reduction process NO is first oxidized and then absorbed together with SO_x in a slurry or a solution. In the reduction process NO is absorbed with SO_x in a liquor containing ferrous ion, which can form an adduct with NO. Usually EDTA (ethylenediamine tetraacetic acid, a chelating compound whose present cost in Japan is about $2700/t) is added to promote the reaction of ferrous ion with NO (Figures 59, 60) (19).

In both cases various reactions, as shown below, occur in the liquor or slurry and result in the reduction of NO_x by SO_2 (or sulfite) to NH_3 through imidodisulfonic acid ($HN(SO_3H)_2$), sulfamic acid (H_2NSO_3H), or a salt or either acid (20).


REDUCTION
HONO
$(HO)_2NH$
$HONH_2$
NH_3
$(HO)_2NSO_3H$
$HONHSO_3H$
H_2NSO_3H
HYDROLYSIS
SULFONATION
$HON(SO_3H)_2$
$HN(SO_3H)_2$
$H(SO_3H)_3$

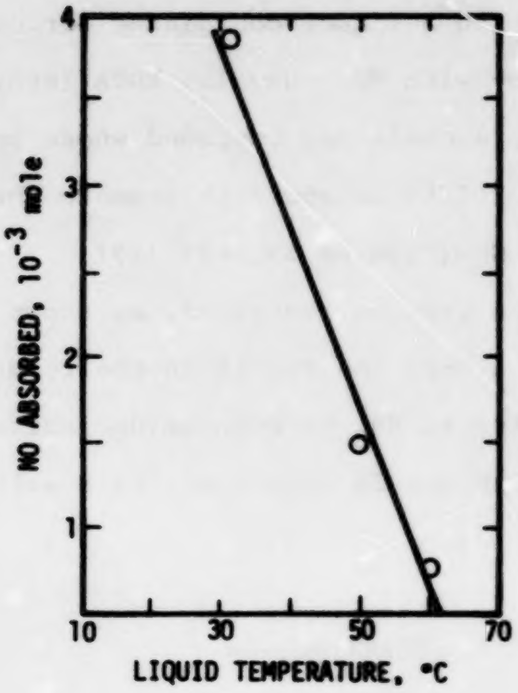


Figure 59. NO absorption in EDTA-Fe(II) liquor (0.01 mole/liter).

(Amount of liquor, 1 liter; gas flow, 1.5 liter/min.; pH of liquor, 5.65; initial NO concentration, 275 ppm)

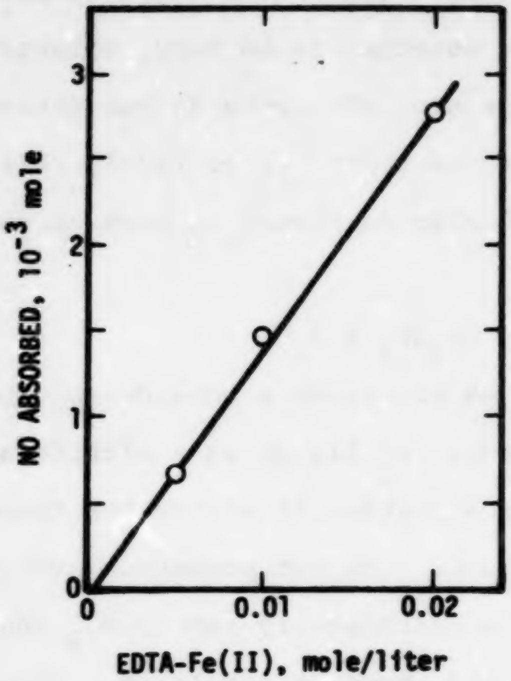


Figure 60. EDTA-Fe(II) concentration and NO absorption at 50°C.

(Amount of liquor, 1 liter; gas flow, 1.5 liter/min.; pH of liquor, 5.65; initial NO concentration, 275 ppm)

NO_x can be reduced to N_2. The reactions are complex but may be simply described:

$NH_2SO_3H + NO_2^- \rightarrow N_2 + HSO_4^- + H_2O$

Tanaka (19) has found that a compound $Na_2SO_3 \cdot 2NO$ is formed when NO is absorbed in an $NaSO_3$ solution. The compound is stable at high pH (above 8) but decomposes to form Na_2SO_4 and N_2O at lower pH. It is likely that in addition to N_2 or NH_3, N_2O also is formed in some of the wet processes.

$Na_2SO_3 \cdot 2NO \rightarrow Na_2SO_4 + N_2O$

In some of the processes a considerable portion of NO_x remains in the resulting liquor as a nitrite and nitrate, which would cause a problem in wastewater treatment.

The advantage of such wet processes over dry processes is that they can simultaneously remove SO_2 and NO_x without problems of dust and ammonium bisulfate. They have not yet been commercialized on a large scale. Five relatively small commercial plants and seven pilot plants are in operation.

TOKYO ELECTRIC - MHI OXIDATION-ABSORPTION PROCESS (21)

MHI has constructed a pilot plant at Minamiyokahama Station, Tokyo Electric Power. The pilot plant has a capacity to treat 100,000 Nm^3/hr of flue gas from an LNG-fired boiler to remove NO_x by a wet process that produces nitric acid. A flowsheet of the process is shown in

Figure 61. Specifications for the system are shown in Table 18.

The flue gas containing about 100 ppm NO_x is cooled with water spray, injected with ozone to oxidize NO to N_2O_5, and then washed with water in an absorber. More than 90 percent of the NO_x is removed when more than 1.7 moles of ozone are used per mole of NO. Resulting dilute nitric acid (about 10 percent concentration) is concentrated to 60 percent for industrial use. Exhaust gas from the absorber is treated with a calcium sulfite slurry and a catalyst to remove residual ozone.

The plant has operated without serious problems, but the process consumes large amounts of ozone and fuel for gas reheating and nitric acid concentration.

KAWASAKI MAGNESIUM PROCESS

Kawasaki Heavy Industries constructed a pilot plant to treat 5000 Nm^3/hr of flue gas from a coal-fired boiler at Takehara Station, Electric Power Development Company. The process was originally designed for SO_2 removal and equimolecular removal of NO and NO_2 with a magnesium hydroxide slurry, followed by oxidation and lime addition to recover gypsum, calcium nitrate, and magnesium hydroxide (1).

A flowsheet of the process is shown in Figure 62. Flue gas is first treated in a venturi scrubber to remove SO_2,

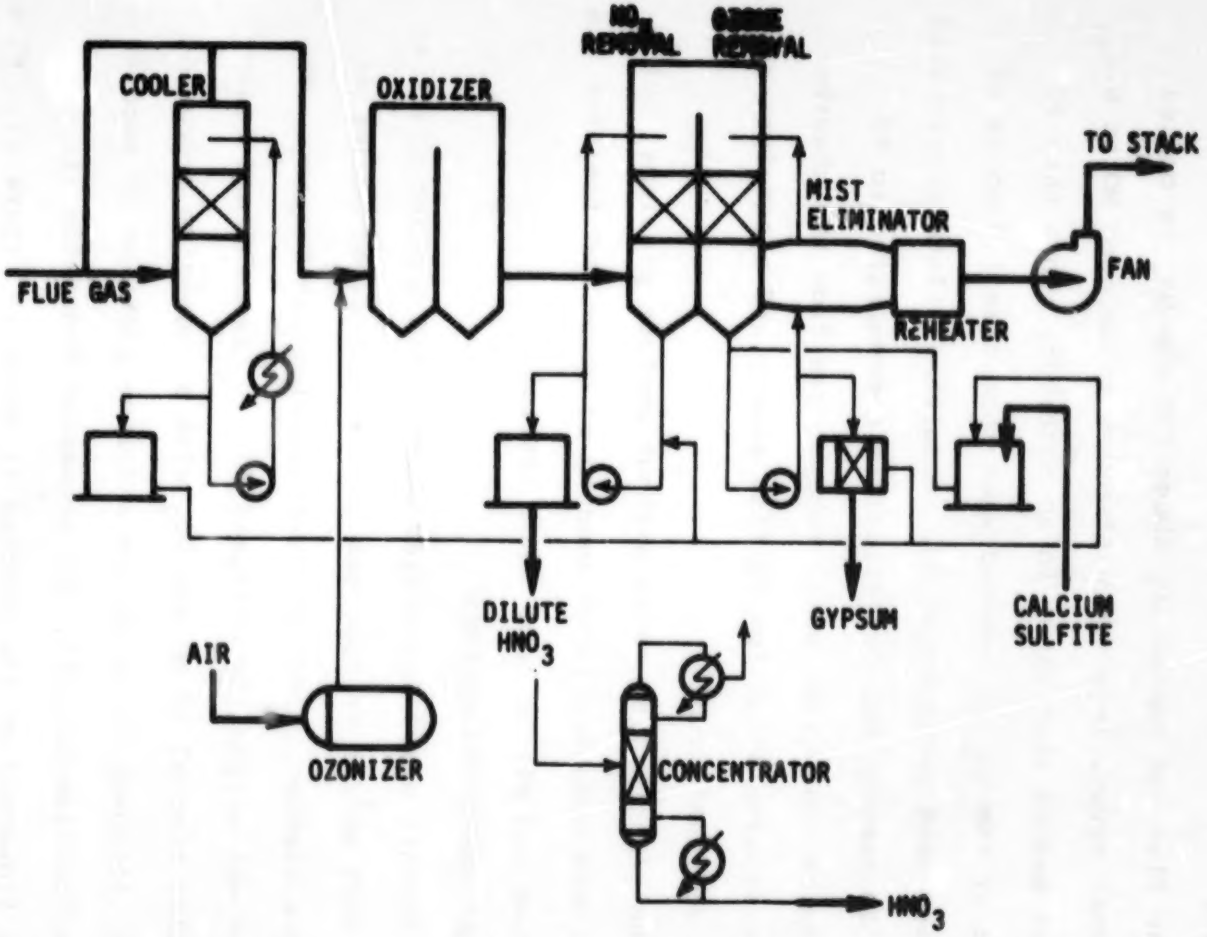

COOLER
OXIDIZER
NO_x REMOVAL
OZONE REMOVAL
TO STACK
MIST ELIMINATOR
FLUE GAS
FAN
REHEATER
DILUTE HNO_3
GYPSUM
CALCIUM SULFITE
AIR
OZONIZER
CONCENTRATOR
HNO_3

Figure 61. Flowsheet of Tokyo Electric - MHI oxidation-absorption process.

Table 18. SPECIFICATIONS FOR THE TEST PLANT

(TOKYO ELECTRIC - MHI PROCESS)

	Material	Structure	Dimensions, m
Cooler	SS 304L	Packed tower	4 x 4 x 11
Oxidizer	SS (plastic coated)	Square tower	4 x 4 x 15
NO_x absorber	SS 304	Packed tower	4 x 4 x 19.5
Ozone absorber	SS 304	Packed tower	4 x 4 x 19.5
Mist eliminator	Polypropylene	Chevron	2.6 x 1.8 x 3
Blower	SS 60 (Impeller)	Centrifugal	370 MW

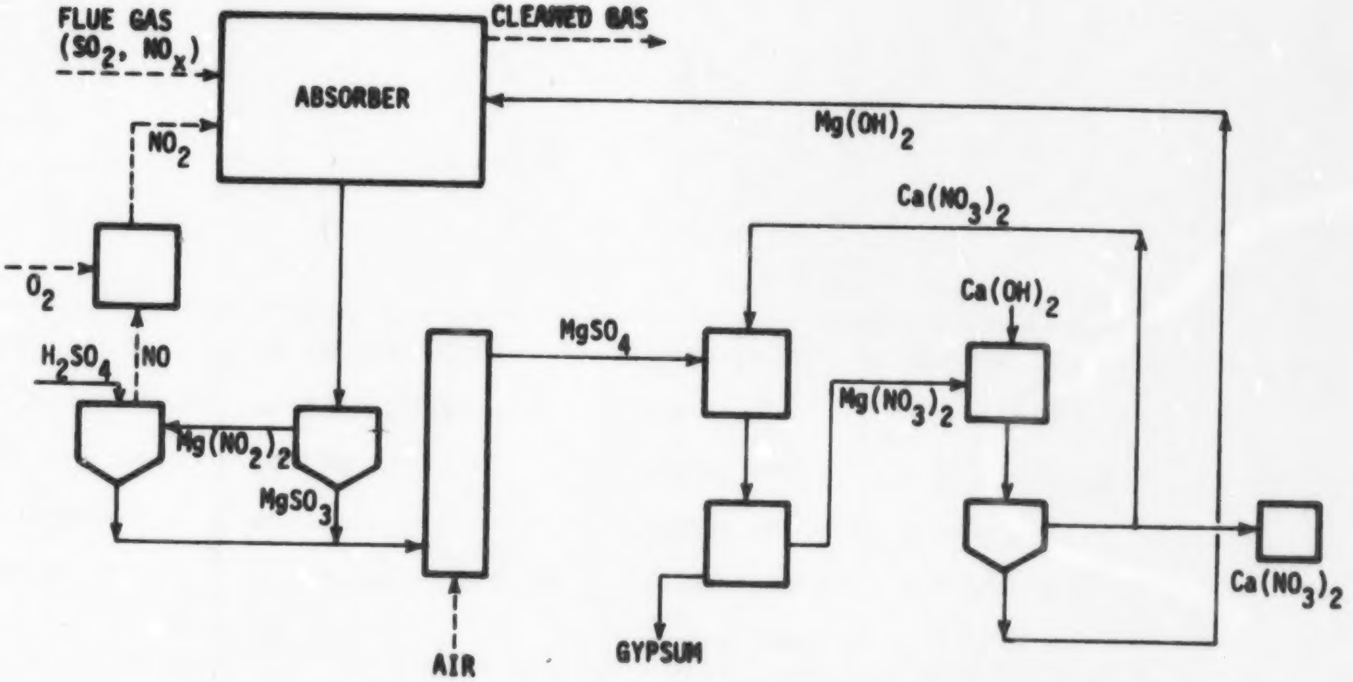

FLUE GAS
(SO_2, NO_x)
CLEANED GAS
ABSORBER
NO_2
O_2
H_2SO_4
NO
$Mg(NO_2)_2$
$MgSO_3$
AIR
$MgSO_4$
GYPSUM
$Mg(NO_3)_2$
$Ca(OH)_2$
$Ca(NO_3)_2$
$Mg(OH)_2$
$Ca(NO_3)_2$

Figure 62. Flowsheet of Kawasaki magnesium process.

using a slurry containing $Mg(OH)_2$, $Ca(OH)_2$, and $Ca(NO_3)_2$ at a pH of 6.2 to 6.5 to produce $CaSO_3$, $MgSO_3$, and $Mg(NO_3)_2$. The desulfurized gas is then mixed with NO_2 and treated in an NO_x absorber with a slurry containing $Mg(OH)_2$ and a small amount of $Ca(NO_3)_2$ at a pH of 6.8 to 7.8 to produce $Mg(NO_3)_2$, $Mg(NO_2)_2$, and a small amount of $CaCO_3$. The discharge from the NO_x absorber is sent to a decomposer and treated with sulfuric acid to release concentrated NO, which is air-oxidized to NO_2 and returned to the absorber. Both discharges from the scrubber and the decomposer are air-oxidized to produce a slurry containing gypsum, $MgSO_4$, and $Mg(NO_3)_2$. The slurry is treated with $Ca(NO_3)_2$ to precipitate gypsum, which is then centrifuged. The separated liquor containing $Ca(NO_3)_2$ and $Mg(NO_3)_2$ is treated with lime to precipitate $Mg(OH)_2$. Most of the liquor containing $Ca(NO_3)_2$ is separated and recycled or recovered as a by-product. $Mg(OH)_2$ containing a small amount of $Ca(NO_3)_2$ is recycled to the scrubber and the absorber.

The absorbing system went into operation in July 1975, and the whole system went into operation in April 1976. The flue gas contains about 1000 ppm SO_2 and 200 to 400 ppm NO_x at 130°C. The volume ranges from 1250 to 6250 Nm^3/hr. More than 95 percent of the SO_2 but less than 50 percent of the NO_x has been removed at a liquid-to-gas ratio of 10.

Tests on ozone-oxidation of NO have been carried out to increase the denitrification ratio. The addition of 1.3 mole or 1.5 mole of ozone to 1 mole of NO increased the removal ratios to 80 and 95 percent, respectively.

Equimolecular absorption is not suitable when the NO_x concentration is low. The limitation on use of calcium nitrate is another drawback of the process.

ABSORPTION-OXIDATION PROCESSES

Nissan Engineering Process (1)

Nissan Engineering, a subsidiary of Nissan Chemical, developed a manganate process and constructed small commercial units for a user and a producer of nitric acid (Table 17). NO_x in waste gases is absorbed by a sodium manganate (or permanganate) solution to form a sodium nitrite solution and manganese dioxide sludge. Sodium nitrite is either sent to a wastewater treatment system or reacted with nitric acid to produce sodium nitrate, which is used for some purpose, and concentrated NO, which is sent to a nitric acid plant. The process is not suitable for flue gas containing SO_2 because the SO_2 consumes the manganate or permanganate.

MON Permanganate Process (1)

Mitsubishi Metal, MKK, and Nippon Chemical Industries, a chemical company producing permanganates, have jointly developed a permanganate process (Table 17).

NO_x is reacted with a potassium permanganate solution to form a potassium nitrate solution and manganese dioxide sludge. The manganese dioxide is converted to potassium permanganate by a conventional process including electrolysis. The potassium nitrate can be used as fertilizer. The process seems expensive. For flue gas treatment, SO_2 should be removed prior to the denitrification because the SO_2 consumes the permanganate.

Kobe Steel Process (1)

Kobe Steel has operated a pilot plant to treat 1000 Nm^3/hr of waste gas from an iron-ore sintering plant. SO_2 is first removed in a calcium chloride solution containing lime. The treated gas is then reacted with a calcium chloride solution containing $Ca(OCl)_2$ as the oxidizing agent. In this reaction, calcium nitrate is formed and chlorine is evolved and then caught by a calcium sulfite slurry from the SO_2 removal system to produce calcium chloride and gypsum. Calcium nitrate is decomposed chemically and reduced to produce N_2. A larger pilot plant (50,000 Nm^3/hr) is near completion. The process requires highly corrosion-resistant materials.

Hodogaya Chemical Process

Hodogaya Chemical has developed a process to remove NO_x by using an $NaClO_3$ solution (Table 17). When the gas contains SO_2, sulfuric acid is also formed.

FUJIKASUI-SUMITOMO SIMULTANEOUS REMOVAL PROCESS (MORETANA PROCESS)

Fujikasui Engineering and Sumitomo Metal Industries jointly developed a sodium scrubbing process for removal of SO_2 and NO_x (Figure 63) and constructed three plants (Table 17). Flue gas containing 1200 to 1300 ppm SO_2 and 240 to 280 ppm NO_x is first cooled by a water spray. Gaseous ClO_2 is added to the gas just before the scrubber and oxidizes NO into NO_2 within 0.5 second. The gas is then introduced into a Moretana scrubber with specially designed perforated plates and is reacted with a sodium hydroxide solution. More than 98 percent of the SO_2 is absorbed to produce sodium sulfite. About 90 percent of the NO_x in the gas is removed. About half of the removed NO_x is converted into N_2 by reaction with sodium sulfite, and the rest is converted into sodium nitrate.

The liquor from the scrubber contains 18 to 22 percent sodium sulfate, 0.5 to 1.8 percent sodium sulfite, 0.4 to 0.8 percent sodium chloride, and 0.4 to 0.9 percent sodium nitrate. The liquor is concentrated to separate most of the sodium sulfate in a crystal form. The remaining liquor is sent to a wastewater treatment system.

Capital cost ranges from \$60 to \$90 per kilowatt. Operating cost, including depreciation (7 years), is roughly \$30 per kiloliter of oil (7 mills per kWh).

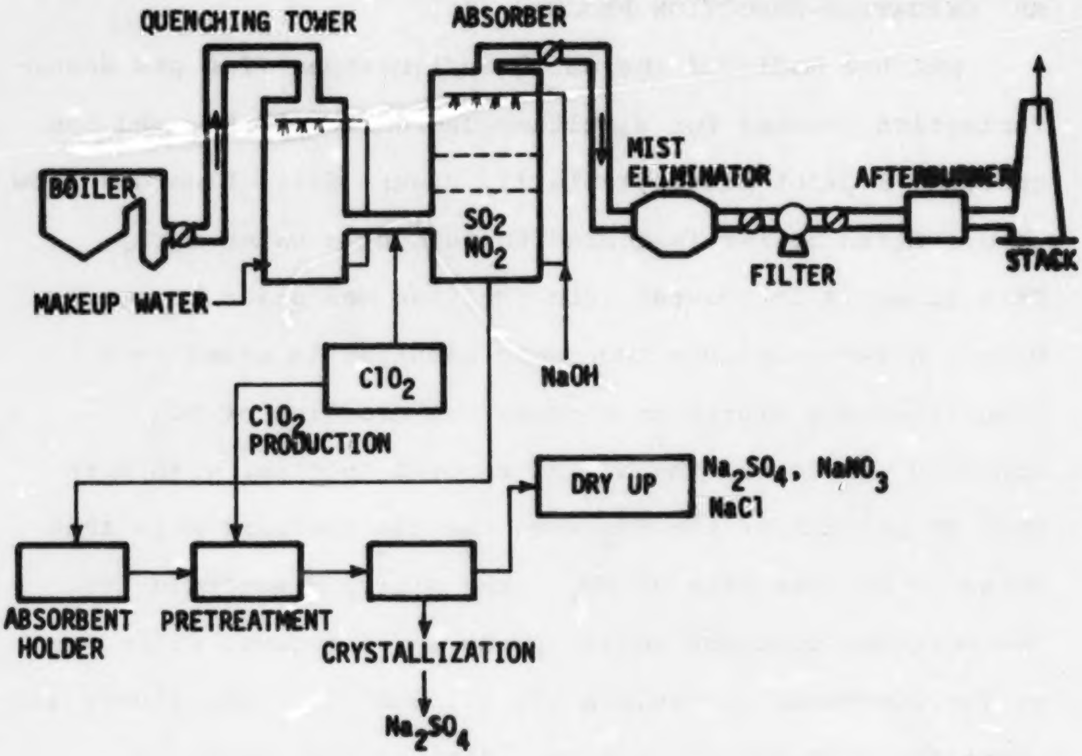
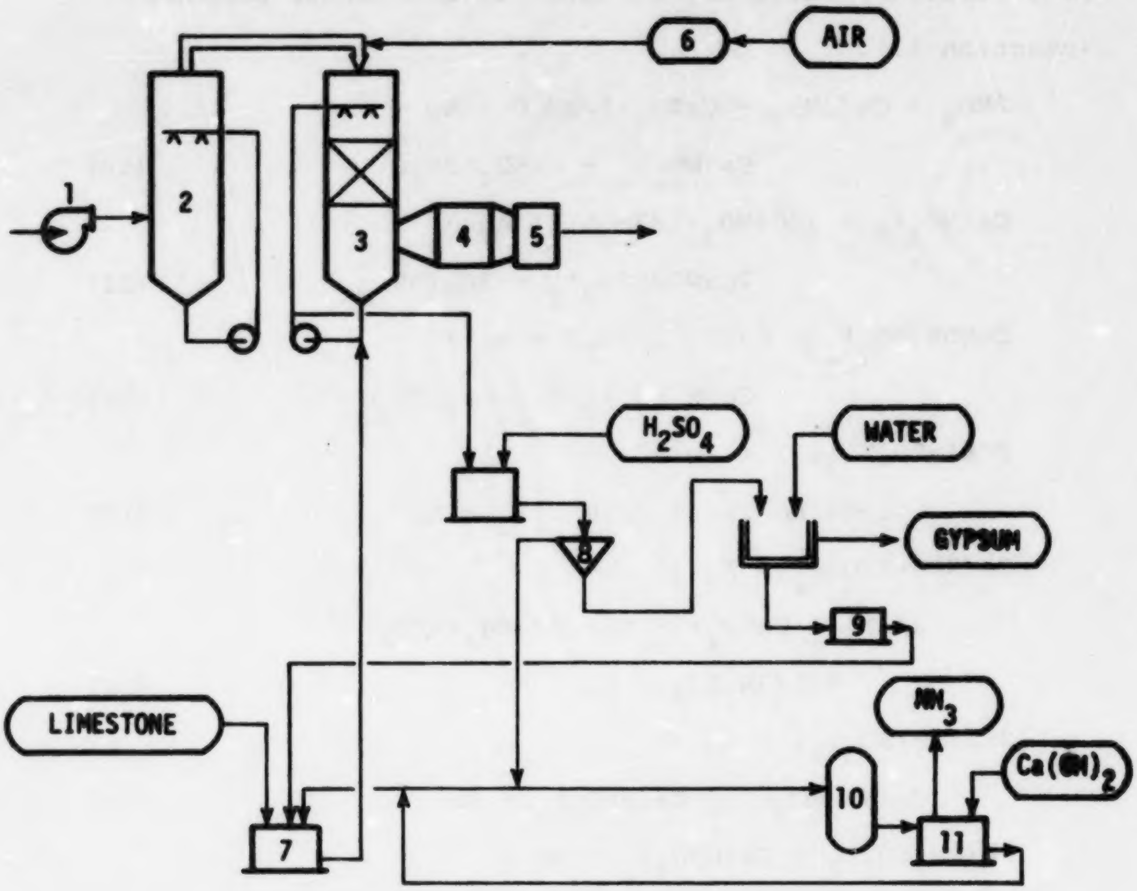

QUENCHING TOWER
ABSORBER
BOILER
MIST ELIMINATOR
AFTERBURNER
SO_2
NO_2
FILTER
STACK
MAKEUP WATER
ClO_2
NaOH
ClO_2 PRODUCTION
DRY UP
Na_2SO_4, $NaNO_3$
NaCl
ABSORBENT HOLDER
PRETREATMENT
CRYSTALLIZATION
Na_2SO_4

Figure 63. Flowsheet of Moretana simultaneous removal process.

Fujikasui recently started tests on ozone oxidation to reduce NO_x to N_2 or NH_3. The process is followed by lime scrubbing to produce gypsum.

MHI OXIDATION-REDUCTION PROCESS (21)

MHI has modified the wet lime/limestone flue gas desulfurization process for simultaneous removal of NO_x and has operated a pilot plant (Table 17, Figure 64). Flue gas from an oil-fired boiler is cooled to 60°C by a water spray. Then ozone is introduced into the flue gas prior to scrubbing. A water-soluble inorganic catalyst is added to a lime/limestone slurry to promote the reaction of NO_2. About 80 percent of the NO_x is removed together with more than 90 percent of the SO_2 when the gas contains more than 3 moles of SO_2 per mole of NO_x. The slurry discharged from the scrubber contains solid gypsum and dissolved nitrogen-sulfur compounds (reactions 10, 11, and 12). The slurry is centrifuged to recover gypsum. Most of the liquor is returned to the absorber after lime or limestone is added. A small portion of the liquor is treated in a decomposer at 100° to 130°C to decompose more than 95 percent of the nitrogen and sulfur compounds (reactions 13 through 16). A small portion of the nitrogen is converted to N_2. Most of it is converted to NH_4HSO_4, which is then treated with lime to recover gypsum and gaseous ammonia, 5 to 10 percent in


6
AIR
1
2
3
4
5
H_2SO_4
WATER
8
GYPSUM
9
LIMESTONE
NH_3
$Ca(OH)_2$
10
11
7

1 Fan
2 Cooling Tower
3 Scrubber
4 Mist Catcher
5 Reheater
6 Ozonizer
7 Absorbent Makeup
8 Thickener
9 Centrifuge
10 Decomposer
11 Neutralizer

Figure 64. MHI simultaneous removal process.

concentration, which may be used for some other purpose (reaction 17).

$$\mathrm{2NO_2 + Ca(OH)_2 + CaSO_3{\cdot}1/2H_2O + Aq \rightarrow Ca(NO_2)_2 + CaSO_4{\cdot}2H_2O} \tag{10}$$

$$\mathrm{Ca(NO_2)_2 + 4(CaSO_3{\cdot}1/2H_2O) + Aq \rightarrow 2CaNOH(SO_3)_2 + 3Ca(OH)_2} \tag{11}$$

$$\mathrm{CaNOH(SO_3)_2 + CaSO_3{\cdot}1/2H_2O + Aq \rightarrow CaNH(SO_3)_2 + CaSO_4{\cdot}2H_2O} \tag{12}$$

$$\mathrm{2Ca[NOH(SO_3)_2] + Aq \rightarrow Ca(NOH{\cdot}HSO_3)_2 + Ca(HSO_4)_2 + Aq} \tag{13}$$

$$\mathrm{Ca(NOH{\cdot}HSO_3)_2 + Aq \rightarrow 2/3N_2 + CaSO_4{\cdot}2H_2) + 2/3NH_4{\cdot}HSO_4 + 1/3H_2SO_4 + Aq} \tag{14}$$

$$\mathrm{2Ca[NH(SO_3)_2] + Aq \rightarrow Ca(NH_2SO_3)_2 + Ca(HSO_4)_2 + Aq} \tag{15}$$

$$\mathrm{Ca(NH_2SO_3)_2 + Ca(HSO_4)_2 + Aq \rightarrow 2NH_4\ HSO_4 + 2CaSO_4{\cdot}2H_2O + Aq} \tag{16}$$

$$\mathrm{NH_4HSO_4 + Ca(OH)_2 + Aq \rightarrow NH_3 + CaSO_4{\cdot}H_2O + Aq} \tag{17}$$

The capital and operating costs for simultaneous removal of NO_x and SO_2 are estimated at about 40 percent more than cost of SO_2 removal only. About 80 percent of the cost increase is accounted for by the ozonizer.

IHI SIMULTANEOUS REMOVAL PROCESS (22)

IHI has been testing an oxidation reduction process at a pilot plant that can treat 5000 Nm^3/hr of flue gas from an oil-fired boiler containing about 1000 ppm SO_2 and 200 ppm NO_x (Figure 65).

The flue gas is cooled, injected with ozone to oxidize NO to NO_2, and treated in a scrubber with a lime/limestone slurry at a pH of 5 to 6 that contains small amounts of $CuCl_2$ and NaCl as catalysts for NO_x absorption (Figures 66 and 67). A lower pH is favorable to NO_x absorption. More than 80 percent of the NO_x and 90 percent of the SO_2 are absorbed, resulting in various reactions in the liquor. The following reactions are assumed to take place:

$$2NO_2 + 4CaSO_3 \rightarrow N_2 + 4CaSO_4$$

$$4NO_2 + 4CaSO_3 + 2H_2O \rightarrow Ca(NO_2)_2 + Ca(NO_3)_2 + 2Ca(HSO_3)_2$$

$$2NO_2 + 3CaSO_3 \rightarrow N_2O + 3CaSO_4$$

$$2NO_2 + 5CaSO_3 + Ca(HSO_3)_2 + H_2O \rightarrow Ca(NH_2SO_3)_2 + 5CaSO_4$$

$$N_2O_5 + 2CaSO_3 + H_2O \rightarrow Ca(NO_3)_2 + Ca(HSO_3)_2$$

About half of the NO_x is reduced to N_2, and half stays in the liquor as nitrate and other compounds. Tests are in progress for further reduction of NO_x to N_2.

OTHER OXIDATION-REDUCTION PROCESSES FOR SIMULTANEOUS REMOVAL

Chiyoda has made a simple modification of the Thoroughbred 101 process to remove NO_x (1). Ozone is added to the gas prior to scrubbing. More than 60 percent of the NO_x is

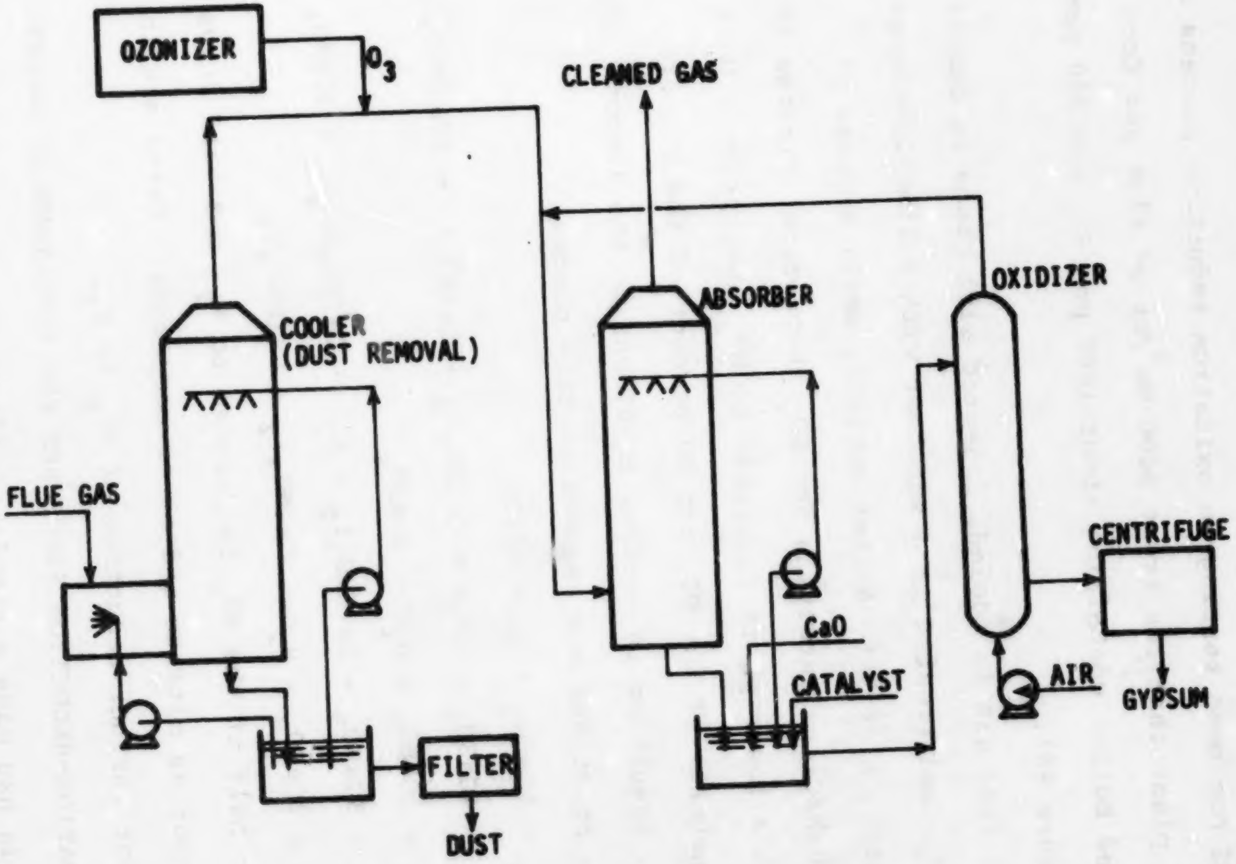

OZONIZER
O_3
CLEANED GAS
OXIDIZER
ABSORBER
COOLER
(DUST REMOVAL)
FLUE GAS
CENTRIFUGE
CaO
CATALYST
AIR
GYPSUM
FILTER
DUST

Figure 65. Flowsheet of IHI simultaneous removal process.

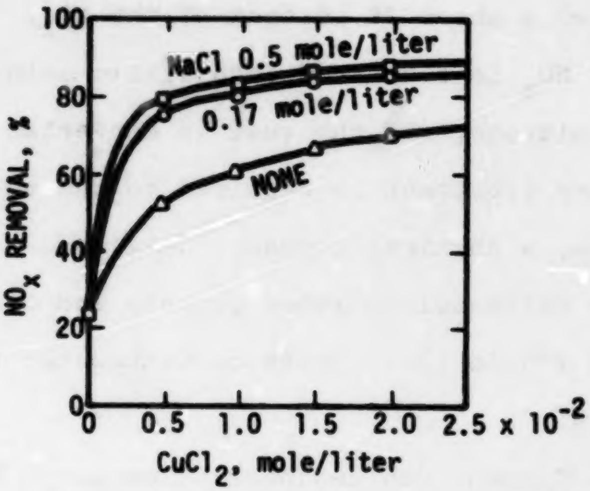


Figure 66. Effects of $CuCl_2$ and NaCl concentrations on NO_x removal efficiency. ($CaSO_3$ 5%, pH 5.5, NO_2/NO_x 95%)

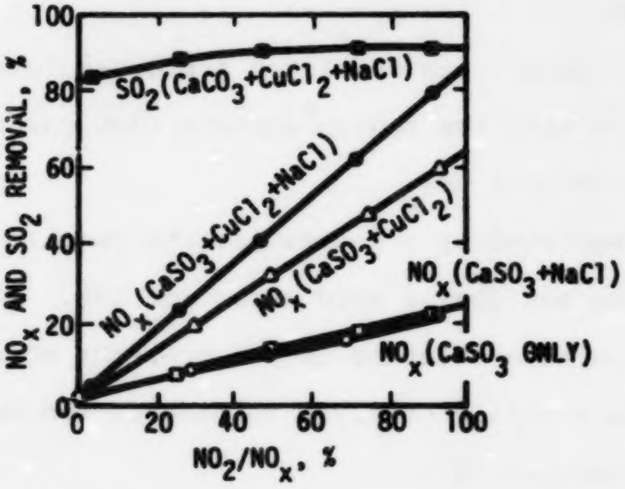


Figure 67. Effects of NO_2/NO_x ratio and additives on removal efficiency.

removed along with about 90 percent of the SO_2. A portion of the removed NO_x is converted into nitric acid, which forms calcium nitrate, and the rest is converted into N_2 and N_2O. Wastewater treatment is required to remove the nitrate.

Osaka Soda, a chemical company, developed a process similar to the Fujikasui-Sumitomo process and constructed a prototype unit (Table 17). Tests on wastewater treatment are in progress.

Shirogane Company, an engineering company, has built a system (Table 17) based on a process similar to the Fujikasui-Sumitomo process except that ozone is substituted for chlorine dioxide. The wastewater containing sodium sulfate and nitrate is sent to a treatment system along with other wastewaters.

KUREHA PROCESS

Kureha Chemical has developed a process to remove NO_x in combination with the sodium acetate flue gas desulfurization process (Figure 68).

SO_2 is absorbed by a sodium acetate solution to produce sodium sulfite and acetic acid (reaction 18). NO is absorbed by a sodium sulfite solution in the presence of acetic acid and a soluble metallic catalyst to produce sodium imidodisulfonate (reaction 19).

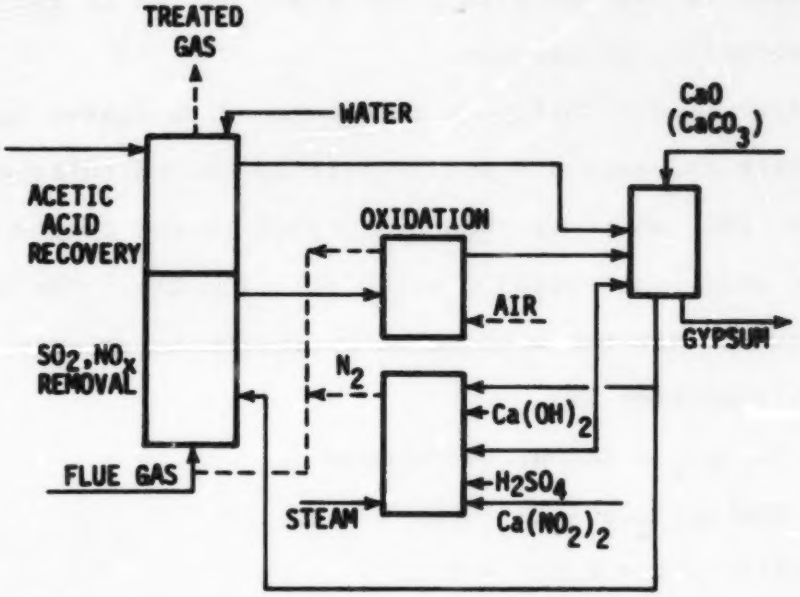

TREATED GAS
WATER
CaO (CaCO$_3$)
ACETIC ACID RECOVERY
OXIDATION
AIR
GYPSUM
SO$_2$,NO$_x$ REMOVAL
N$_2$
Ca(OH)$_2$
FLUE GAS
H$_2$SO$_4$
STEAM
Ca(NO$_2$)$_2$

Figure 68. Flowsheet of Kureha simultaneous removal process.

$$SO_2 + 2CH_3COONa + H_2O \rightarrow Na_2SO_3 + 2CH_3COOH \qquad (18)$$

$$2NO + 5NaSO_3 + 4CH_3COOH \rightarrow 2NH(SO_3Na)_2 + Na_2SO_4 + 4CH_3COONa + H_2O \qquad (19)$$

The remaining sodium sulfite is air-oxidized into sulfate. The sulfate is treated with calcium acetate as in the flue gas desulfurization process.

Sodium imidodisulfonate is reacted with slaked lime to precipitate and separate sodium calcium imidodisulfonate (reaction 20), which is then hydrolyzed in the presence of sulfuric acid into sulfamic acid (reaction 21). The sulfamic acid is treated with calcium nitrite to release nitrogen (reaction 22).

$$NH(SO_3Na)_2 + Ca(OH)_2 + CH_3COOH \rightarrow NNa(SO_3)_2Ca + CH_3COONa + 2H_2O \qquad (20)$$

$$2NNa(SO_3)Ca + H_2SO_4 + 2H_2O \rightarrow 2NH_2SO_3H + Na_2SO_4 + 2CaSO_4 \qquad (21)$$

$$2NH_2SO_3H + Ca(NO_2)_2 \rightarrow 2N_2 + CaSO_4 + H_2SO_4 + 2H_2O \qquad (22)$$

Kureha has been operating a pilot plant with a capacity to treat 5000 Nm^3/hr of flue gas from an oil-fired boiler. The process seems fairly complicated with many reaction steps. Recently, the sodium imidodisulfonate has been found useful as a builder of detergents to replace sodium tripolyphosphate, which has been causing eutrophication problems.

Tests have been in progress on the effect of the disulfonate on the environment. Possible commercial use of the disulfonate will make the process useful.

MITSUI SHIPBUILDING PROCESS

Mitsui Shipbuilding has developed a simultaneous removal process that produces concentrated SO_2, which can be used in sulfuric acid production (Figure 69).

Flue gas is treated with a ferrous compound solution containing EDTA which absorbs both SO_2 and NO.

A portion of the ferrous ion is converted to ferric ion by the oxygen in flue gas. The ferric ion in the absorbed liquor is then reduced to ferrous ion by electrolysis, and the liquor is sent to a stripper, where it releases concentrated SO_2 and NO by steam distillation. The NO is reduced to N_2; the SO_2 is used in sulfuric acid production. The liquor from the scrubber is returned to the absorber. In tests with a pilot plant (150 Nm^3/hr) about 95 percent of the SO_2 and 85 percent of the NO_x were removed at a liquid-to-gas ratio of 1 liter/Nm^3.

It is estimated that the plant cost is $80 million for a 67-megawatt plant. EDTA consumption per year is 300 to 400 tons at a cost of $500,000 to 600,000.

By using H_2S in the reduction step, elemental sulfur may be produced. Tests with a larger plant are required for further evaluation.

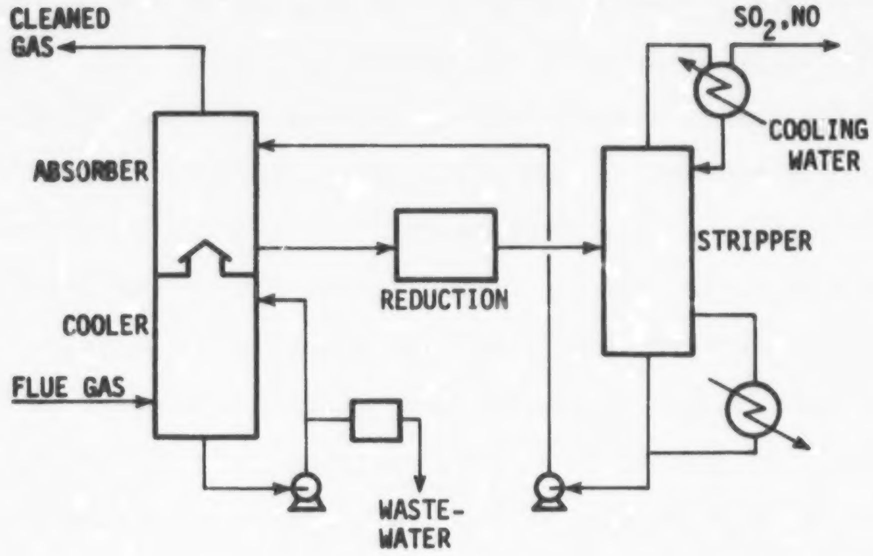

CLEANED GAS
SO_2, NO
ABSORBER
COOLING WATER
STRIPPER
REDUCTION
COOLER
FLUE GAS
WASTE-WATER

Figure 69. Flowsheet of Mitsui Shipbuilding process.

CHISSO PROCESS (CEC PROCESS)

Chisso Engineering, a subsidiary of Chisso Corporation, has developed a process for simultaneous removal of SO_2 and NO_x from flue gas by ammonia scrubbing using a catalyst (chelating compound) to produce ammonium sulfate. A pilot plant treating 300 Nm^3/hr of flue gas from an oil-fired boiler has been operating (Figure 70).

SO_2 and NO_x from the flue gas is absorbed in an ammoniacal solution containing a soluble catalyst to reduce the absorbed NO_x to NH_3 by ammonium sulfite and bisulfite, which are formed from SO_2 and ammonia. Most of the catalyst is separated from the product solution, containing ammonium sulfate and sulfite and the intermediate compounds. The solution is oxidized by air and then heated to convert the intermediate compounds into ammonium sulfate. The product solution is concentrated in an evaporator to crystallize ammonium sulfate, which is separated by a centrifuge. The mother liquor, which contains a small amount of the catalyst, is returned to the catalyst separation step. The over-all reaction may be expressed as follows:

$$2NO + 5SO_2 + 8NH_3 + 8H_2O = 5(NH_4)_2SO_4$$

At an NO_x concentration of 300 ppm it is desirable to have more than 1200 ppm SO_2 in the flue gas in order to recover 80 percent of the NO_x.

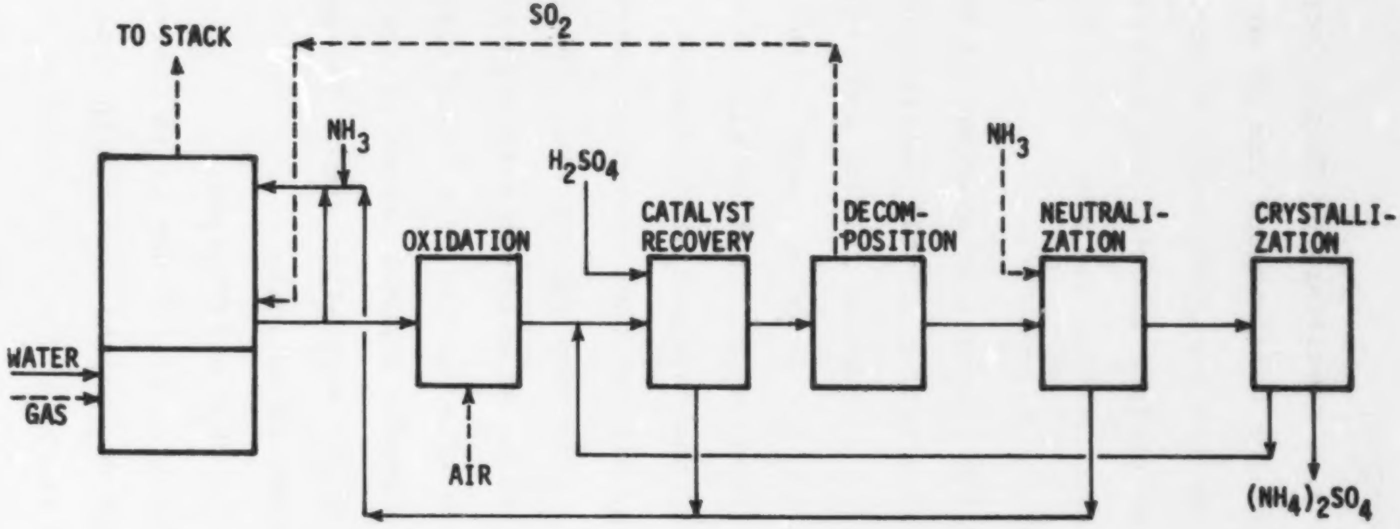

TO STACK
SO_2
NH_3
H_2SO_4
NH_3
WATER
GAS
OXIDATION
CATALYST RECOVERY
DECOM-POSITION
NEUTRALI-ZATION
CRYSTALLI-ZATION
AIR
$(NH_4)_2SO_4$

Figure 70. Flowsheet of CEC process.

Reaction of NO_x with the sulfite liquor is not rapid, and the removal ratio has ranged from 70 to 80 percent. The use of a dilute liquor is favorable for absorption but necessitates much evaporation for ammonium sulfate recovery. Therefore, NO_x removal of about 70 percent, using a moderate sulfite concentration, may be suitable. The catalyst is not affected by nickel and vanadium derived from the flue gas. Chisso estimates that the cost of simultaneous removal of SO_2 and NO_x is about 40 percent more than the cost of SO_2 removal only.

The process has the advantage of producing ammonium sulfate by use of both SO_2 and NO_x. Plume formation common to ammonia scrubbing processes might be a problem.

ASAHI CHEMICAL PROCESS

Asahi Chemical Company has been testing a reduction process with a pilot plant (600 Nm^3/hr). A flowsheet of the process is shown in Figure 71. A flue gas containing 1250 ppm SO_2, 3 to 4 percent O_2, and 200 ppm NO_x passes through a sieve-tray absorber and is treated with a sodium sulfite solution at a pH of 6.3, containing EDTA and ferrous ion. More than 80 percent of the NO_x is absorbed and forms an adduct with ferrous ion and EDTA, whereas more than 90 percent of the SO_2 is absorbed and reacts with the sulfite.

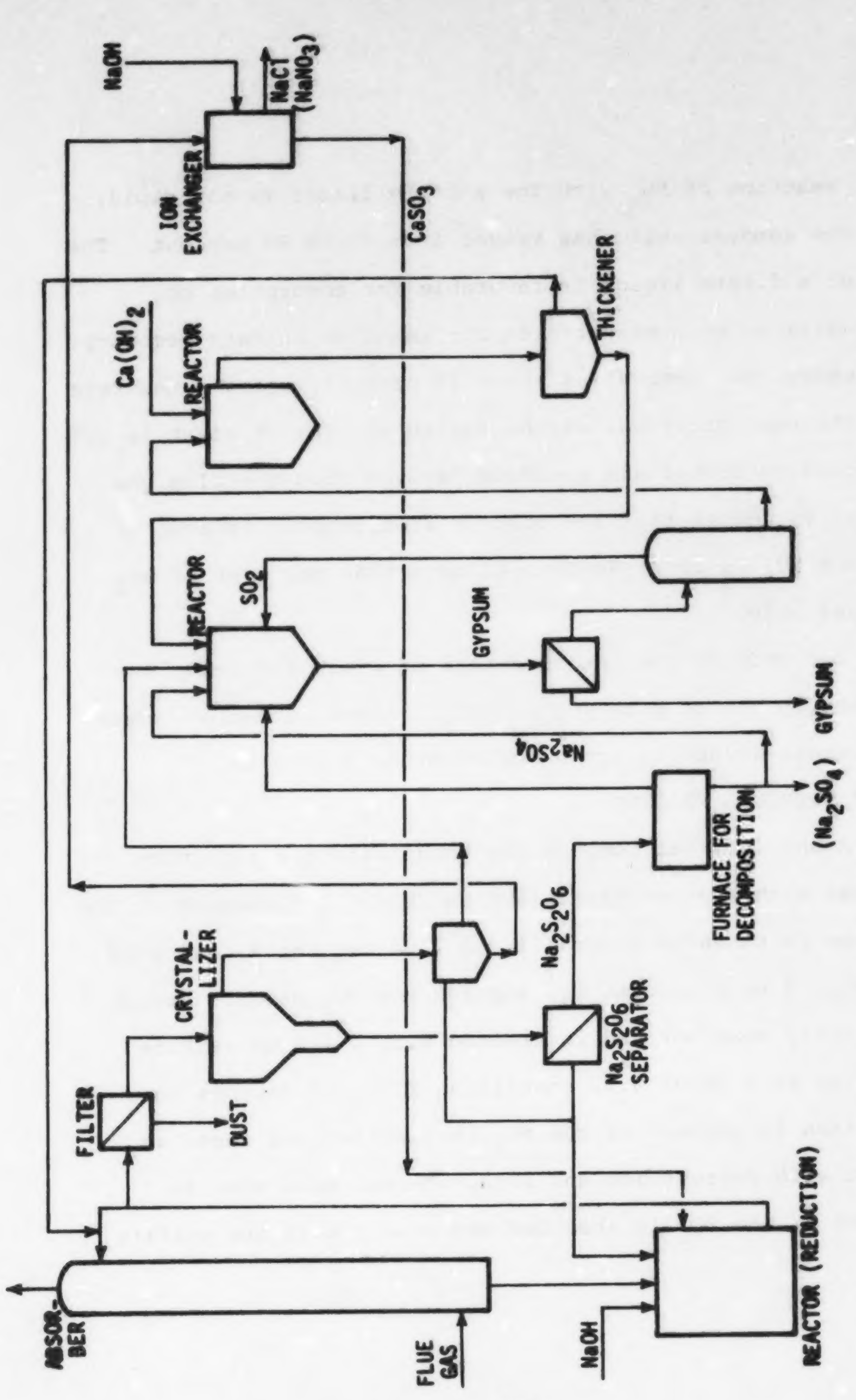

ABSORBER
FLUE GAS
NaOH
REACTOR (REDUCTION)
FILTER
DUST
CRYSTALLIZER
$Na_2S_2O_6$ SEPARATOR
$Na_2S_2O_6$
FURNACE FOR DECOMPOSITION
(Na_2SO_4)
GYPSUM
Na_2SO_4
REACTOR
SO_2
GYPSUM
$Ca(OH)_2$
REACTOR
THICKENER
$CaSO_3$
ION EXCHANGER
NaOH
NaCl ($NaNO_3$)

Figure 71. Flowsheet of Asahi Chemical reduction process.

The NO adduct reacts with the sulfite to form sodium sulfate and nitrogen by the following reaction:

$$Fe^{++} \cdot EDTA \cdot NO + Na_2SO_3 \rightarrow Fe \cdot EDTA + 1/2N_2 + Na_2SO_4$$

Most of the resulting liquor is returned to the absorber. A portion is sent to a crystallizer, where sodium dithionate $Na_2S_2O_6 \cdot 2H_2O$ iTs crystallized. The dithionate is separated and heated at 300°C to be decomposed to Na_2SO_4 and SO_2, both of which are sent to a reactor and reacted with calcium sulfite to precipitate gypsum.

$$Na_2S_2O_6 \cdot 2H_2O \rightarrow Na_2SO_4 + SO_2 + 2H_2O$$

$$Na_2SO_4 + SO_2 + CaSO_3 + H_2O \rightarrow 2NaHSO_3 + CaSO_4$$

$$2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3$$

The sodium bisulfite solution formed by the reaction is treated with lime to precipitate calcium sulfite and to regenerate sodium sulfite. The former is sent to the reactor, and the latter is recycled to the absorbing system. Chlorine, derived from the fuel, accumulates in the scrubbing liquor and can be eliminated by ion exchange. Asahi Chemical has had much experience in ion exchange.

Asahi Chemical estimates that the plant cost for a 500,000 Nm^3/hr unit (160 MW equivalent) is \$16 million and that requirements for the treatment of 10,000 Nm^3 of gas containing 2000 ppm of SO_2 are as follows:

$Ca(OH)_2$	6.7 kg
$FeSO_4 \cdot 7H_2O$	1.0 kg
EDTA	1.0 kg
NaOH	4.2 kg
Oil (Gas reheating)	30 kg
Oil (Thermal decomposition)	5 kg
Steam	60 kg
Cooling water	6 tons
Power	150 kWh

The system is a combination of several feasible unit processes. Operating data from a larger pilot plant may be needed for a reliable evaluation.

SECTION 5

EVALUATION AND DISCUSSION

SIGNIFICANCE OF FLUE GAS DENITRIFICATION

The present development in flue gas denitrification in Japan is a result of the stringent ambient standard for NO_2, 0.02 ppm daily average of hourly values, about equivalent to 0.01 ppm yearly average. The ambient NO_2 concentrations in large cities such as Tokyo and Osaka range from 0.02 to 0.05 ppm (yearly average) and are not higher than concentrations in Los Angeles and Chicago. With the approach of the time limit for attaining the standard -- 1978 in most regions and 1981 in polluted regions -- doubts have been raised as to the necessity for such a stringent standard because it will be difficult to attain and will require tremendous expenditures.

In any case, it is necessary to develop further technologies for both flue gas denitrification and combustion modification as long as consumption of fossil fuels continues to increase. Particularly in countries where coal consumption is increasing, denitrification will be needed sooner or later because it is difficult to reduce the NO_x in the flue gas from coal burning to below 400 ppm by combustion modification without increasing the particulates. On the other hand, NO_x concentrations in flue gas from burning of gas or oil can be reduced to 50 or 100 ppm by combustion modification.

Because the denitrification processes are not yet fully developed and are still too expensive to be used in treating dirty gases containing much SO_x and dust, industries in Japan have been moving toward the use of clean fuels such as LNG, kerosene, naphtha, and low-sulfur oil (less than 0.3% sulfur). The clean fuels, however, are expensive and are limited in supply. Under the stringent NO_x control in Japan, flue gas denitrification will be indispensable, particularly for new plants, even though clean fuels are burned with combustion modifications.

COMBINATION OF FLUE GAS DESULFURIZATION AND DENITRIFICATION

Clean gas can be easily denitrified with more than 90 percent efficiency by SCR processes using a fixed bed of a catalyst that has more than 2 years life. Many processes for treatment of a dirty gas have been developed and are shown schematically in Figure 72.

System 1 in the figure is an ideal dry process for simultaneous removal of SO_x and NO_x by which a flue gas at a normal temperature of 140°C, after passing through an

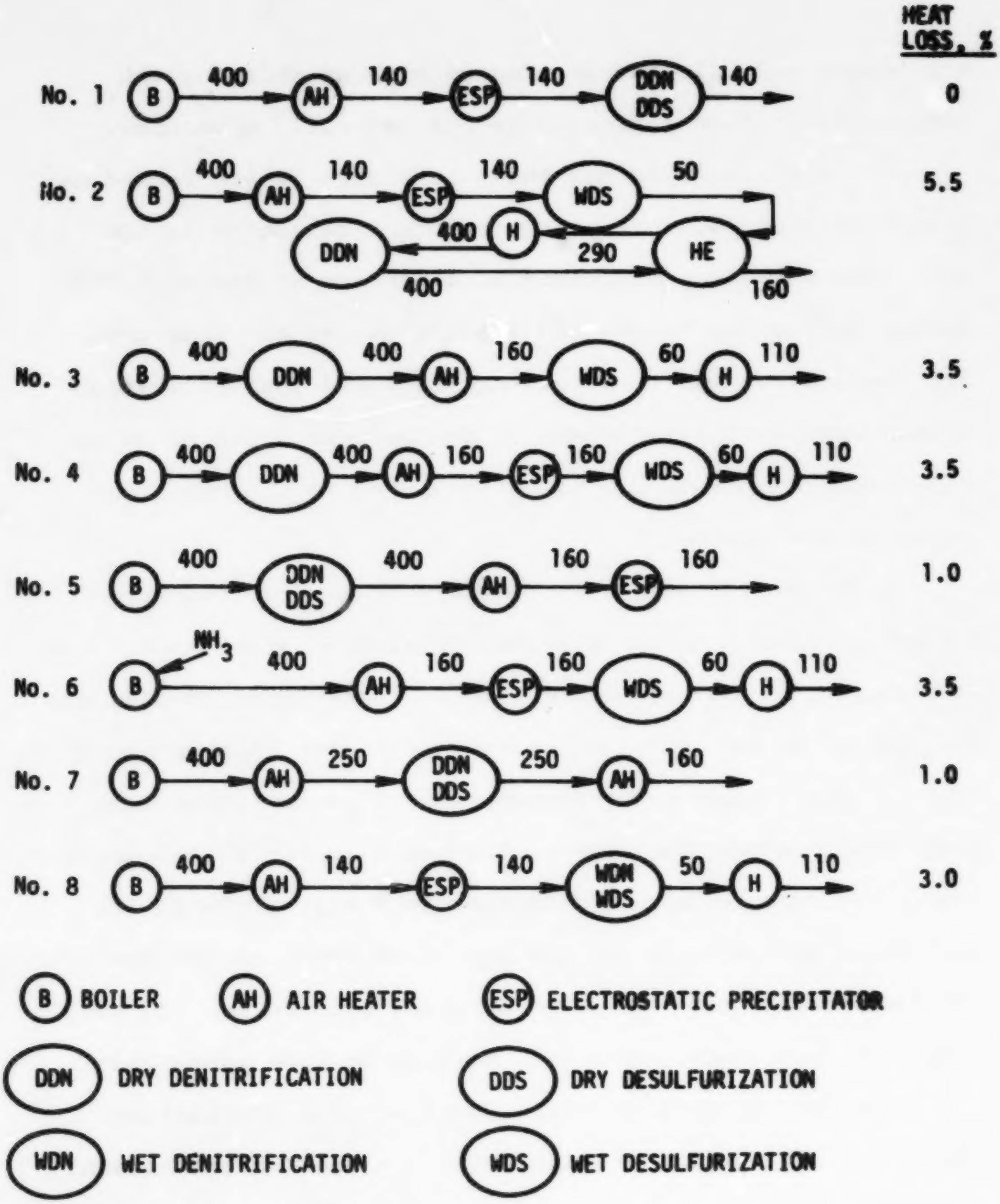

HEAT LOSS, %
No. 1 B 400 AH 140 ESP 140 DDN DDS 140 — 0
No. 2 B 400 AH 140 ESP 140 WDS 50 HE 290 H 400 DDN 400 HE 160 — 5.5
No. 3 B 400 DDN 400 AH 160 WDS 60 H 110 — 3.5
No. 4 B 400 DDN 400 AH 160 ESP 160 WDS 60 H 110 — 3.5
No. 5 B 400 DDN DDS 400 AH 160 ESP 160 — 1.0
No. 6 NH3 B 400 AH 160 ESP 160 WDS 60 H 110 — 3.5
No. 7 B 400 AH 250 DDN DDS 250 AH 160 — 1.0
No. 8 B 400 AH 140 ESP 140 WDN WDS 50 H 110 — 3.0
B BOILER
AH AIR HEATER
ESP ELECTROSTATIC PRECIPITATOR
DDN DRY DENITRIFICATION
DDS DRY DESULFURIZATION
WDN WET DENITRIFICATION
WDS WET DESULFURIZATION
H HEATER
HE HEAT EXCHANGER

Figure 72. Combination of denitrification and desulfurization (Figures show gas temperature, °C).

air heater and ESP, may be treated without changing the temperature. Such a process is not yet fully developed.

The heat requirements shown in Figure 72 are caused by losses in heat recovery and by required reheating of the gas. The amount is expressed as a percent of the heat for boiler operation, taking the loss in System No. 1 as zero. Heat needed to operate desulfurization and denitrification units, such as the heat used to concentrate a liquor or to regenerate the catalyst, is not included in the heat loss shown in the figure.

Systems 2 through 7 include dry denitrification processes -- ammonia reduction with or without a catalyst. For these systems, the air heater outlet temperature of flue gas is assumed to be 160°C, which is 20°C higher than in System No. 1. This temperature accounts for 1 percent heat loss because ammonium bisulfate will deposit in the air heater at the lower temperature. The temperature may vary with SO_3 and NH_3 concentrations of the gas, with types of air heater (or heat exchanger), and with cleaning procedures. In many cases the gas temperature will have to be kept above 160°C.

System 2 shows a combination of wet desulfurization (WDS) and dry denitrification (DDN), as used in the Hitachi Shipbuilding process, which has been operated commercially in Japan since 1975. In addition to a standard air heater, the process requires a heat exchanger and much energy for gas heating, although the process seems feasible for treating flue gases from oil burning.

In systems 3 and 4, flue gas from the air heater at 400°C is first subjected to SCR and then to wet desulfurization. A considerable energy savings is attained compared with System 2. System 3 uses a moving-bed reactor, as in the Kurabo process. Treatment of flue gas from oil burning may not require an ESP because most of the dust is caught on the catalyst bed, but the catalyst must be treated continuously or intermittently. Treatment of flue gas from coal burning will require an ESP or other dust removal facility ahead of the reactor. System 4 uses a parallel-passage reactor like the Japan Gasoline - Shell reactor. The catalyst bed is hardly contaminated by the dust, although an ESP may be needed after the air heater. The advantage of the parallel-passage reactor may be greater if it can treat flue gas from coal burning without using a hot ESP ahead of the reactor.

System 5 shows simultaneous SO_2 and NO_x removal at 400°C, as in the Shell process. A dry flue gas desulfurization process is usually much more expensive than a wet process, although it does not require gas reheating. In system 5, however, the disadvantage might be compensated for by the capability of simultaneous SO_2 and NO_x removal.

System 6 shows ammonia injection into the boiler without a catalyst, followed by wet desulfurization. The process is simple and is less expensive than others, but even a large-scale system may not easily attain more than 50 percent NO_x removal.

For Systems 3 through 6, any fluctuating gas temperature resulting from a change of the boiler load will present a problem. In Systems 3 through 5 ammonium bisulfate may deposit on the catalyst and poison it when the temperature drops below 350°C. In order to maintain the gas temperature, it may be necessary to install an auxiliary burner or a device to take some high-temperature gas from the boiler. The problem is more serious for the ammonia injection process without a catalyst because the process has a narrow range of suitable reaction temperatures around 970°C. Although the addition of hydrogen with ammonia can reduce the temperature to 870°C, use of hydrogen at power plants may not be practicable. The process may be better suited to boilers that have smaller load fluctuations.

System 7 is a dry simultaneous removal process using activated carbon, such as the Unitika process. More than 90 percent of the SO_2 and the NO_x is removed with little heat loss. Actually, a considerable amount of heat would be required for the removal of the SO_2 from the carbon. The required reaction temperature of 250°C is not favorable because two air heaters may be needed, as shown in Figure 72. For the treatment of flue gas from coal burning, an ESP will be required ahead of the reactor. The activated carbon, reactive at 100° to 150°C, (developed by Hitachi, Limited) permits treatment similar to that by System 1. However, considerable amounts of ammonium bisulfite and sulfate may deposit on the carbon and necessitate frequent regeneration.

System 8 is a wet simultaneous removal process. The wet process has advantages over the dry process in achieving simultaneous removal of more than 80 percent of the NO_x and 90 percent of the SO_2 without the problems of dust and ammonium bisulfate. The process involves some problems, as described in Section 4, and has not yet been commercialized on a large scale.

Many other processes are under development, but they may not be as useful in treating large amounts of dirty flue gas as those mentioned above.

Consumption of ammonia would present a problem if the dry processes were to be used extensively. It is estimated that about 400,000 tons of ammonia will be consumed yearly to attain the ambient standard by dry processes alone. This amount is about half the total annual consumption of nitrogen fertilizers in Japan. If the dry processes should be used widely throughout the world, a serious shortage of nitrogen fertilizer could occur, affecting the supply of food. Since it is expected that the need for denitrification will increase in many countries, development should be concentrated not only the dry processes but also on the wet processes capable of producing ammonia or nitrogen fertilizers.

Both the MHI and Chisso processes can produce ammonia from NO_x by use of SO_2 as the reducing agent. For power plants where no by-product is desired, the ammonia may be fed to the boiler to convert a portion of the NO_x in the flue gas to N_2 without a catalyst and thus facilitate simultaneous removal by a wet process because a higher SO_2/NO_x ratio is more suitable for these processes.

In any case, combustion modification should be carried out for NO_x abatement because it is much more economical than flue gas denitrification and will enable the denitrification to be accomplished with less expense when the NO_x concentration of the gas is low.

SECTION 6

REFERENCES

Descriptions in this report are based primarily on the authors' visits to the denitrification plants, their discussions with the users and developers of each process, and data made available by them. In addition, the following publications were used as references:

1. Ando, J., H. Tohata, and G. Isaacs. NO_x Abatement for Stationary Sources in Japan, EPA-600/2-76-013h (in English). January 1976.

2. Ando, J., and H. Tohata. NO_x Abatement Technology in Japan, EPA-R2-73-284 (in English). June 1973.

3. Yamagishi, K., et al. Low NO_x Burner Developed by Tokyo Gas Co., Journal of the Japan Society of Mechanical Engineers, Vol. 77, No. 663. 1974. p. 225.

4. Idehara, S. NO_x Control Techniques Developed by Kawasaki Heavy Industries Co., Environmental Creation, Vol. 6, No. 4. 1976. p. 62.

5. Kanamori, S. Low NO_x Burner Developed by Volcano Co., Heat Management and Pollution Control, Vol. 26, No. 12. 1974. p. 47.

6. Nagaoka, M. NO_x Control Techniques Used in Utility Boilers, Environmental Creation, Vol. 6, No. 4. 1976. p. 153.

7. Japan Environment Agency, Control Techniques used for NO_x Emissions from Stationary Sources. March 1975.

8. Kobayashi, H., and K. Huruyaho. Techniques for NO_x Reduction in Boilers, Environmental Creation, Vol. 6, No. 4. 1976. p. 87.

9. Mizobuchi, I. Concrete Measures for NO_x Reduction. Symposium on Pollution Control, Japan Management Association. June 1974.

10. Tokyo Metropolis Bureau of Environmental Protection, Basic Investigation on NO_x Control Techniques. March 1975.

11. Tokyo Metropolis Bureau of Environmental Protection, Investigation on Fuel NO_x Conversion Ratio. March 1975.

12. Report of Nitrogen Oxides Investigation Committee, Japan Environment Agency. October 1975.

13. Atsukawa, M., et. al. Development of NO_x Removal Processes with Catalyst for Stationary Combustion Facilities, Mitsubishi Juko Giho, Vol. 13, No. 2. 1976.

14. Shima, T. Problems of Denitrification Facility for Boilers, Netsukanri to Kogai, Vol. 27, No. 12.

15. Lyon, R.K., and J.P. Longwell. Selective, Noncatalytic Reduction of NO_x by NH_3, EPRI NO_x Seminor, San Francisco (Feb. 1976).

16. Ninomiya, N. Simultaneous Removal of NO_x and SO_2 by Activated Carbon, Report of Takeda Chemical. 1975.

17. Seki, M. et al. Ammonium Hallide Activated Carbon Catalyst to Decompose NO_x in Stack Gases at Low Temperatures around 100°C. American Chemical Society, Chicago. August 1975.

18. Kawakami, W., and K. Kawamura. Treatment of Oil-fired Flue Gas by Electron Beam, Denkikyokai Zasshi, 29. December 1973.

19. Tanaka, T., M. Koizumi, and Y. Ishihara. Wet Process for Nitrogen Oxides Removal from Flue Gases (Part 3). Denryoku Chuokenkyujo Hokoku 275017. April 1976.

20. Audrieth, L.F., et al. Sulfamic Acid, Sulfamide and Related Aquo-ammonosulfuric Acids, Symposium on the Chemistry of Liquid Ammonia Solutions. American Chemical Society, Milwaukee. September 1938.

21. Atsukawa, M., et al. Development of Wet-type NO_x Removal Processes. Mitsubishi Juko Giho, Vol. 13, No. 2. 1976.

22. Yamada, S., T. Watanabe, and H. Uchiyama. Bench-scale Tests on Simultaneous Removal of SO_2 and NO_x by Wet Lime and Gypsum Process. Ishikawajima-Harima Engineering Review. January 1976.